AN INVESTIGATION INTO THE FORMATION OF WAX EMULSIONS.

BY

JOHN MICHAEL CHARLES ROBERTS.

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Summary.

Wax emulsions have been part of every day life for many years. They find use in a wide variety of products such as furniture and floor polishes, aerosol sprays, cosmetic products, and are used to coat various articles from paper to fruit. Occasionally, substandard batches are produced and the reasons for the defects are not always known. Procedures for the recovery of such batches are far from perfect and, because the raw materials have a relatively high value, considerable loss to a manufacturer can result. A review of the literature over approximately sixty years indicated that little specific information had been published about wax emulsions, and that established emulsion manufacturing techniques were virtually unchanged over the same period. Therefore the following objectives were formulated:-

A. The Investigation of a satisfactory means for assessing product quality.
B. The Definition and ranking of the system variables.
C. The Investigation into the 'mechanism' of wax emulsification.
D. The Application of the study findings to existing commercial methods for wax emulsion manufacture, including the reworking of unsatisfactory batches.

The study produced the following conclusions:-

A. The most important criteria of wax emulsion quality are those of appearance and stability. Appearance is viewed subjectively by the creaming, translucency and the viscosity of the product, and is best assessed either by gravimetric determination of the percentage of disperse phase above 10 microns or by microscopic examination. Stability is a parameter of product shelf-life and new freeze-thaw and titration techniques have been developed which give rapid and reliable results.

B. Although fourteen variables have been identified and investigated in the wax emulsification process, only three are determined as important. These are:-

  a. Level and type of emulsifier(s).
  b. Degree of wax saponification if required as part of the emulsifier system.
  c. Extent and type of agitation provided during emulsification.

C. Wax emulsification, using the most common method of surface addition at atmospheric pressure, proceeds via the formation of wax filaments which, after being drawn below the water surface, are converted to droplets by shear forces. These forces are applied by velocity differentials between wax and water, in turn induced by agitation. Wax emulsification differs from conventional liquid/liquid processes because a phase change is usually involved. Droplet formation must occur prior to this change or a substandard emulsion results.

D. Some basic manufacturing rules are proposed to reduce the proportion of substandard batches. When these do occur however, those containing waxes that may be liquified below the normal boiling point of water, may be reworked by reheating and mechanical homogenisation. Unsatisfactory products containing waxes of higher melting ranges can only be reworked using the technique of pressure emulsification. Further improvements to manufacturing methods should be possible. Continuous processing and pressure emulsification are concluded to be areas where future research might prove most rewarding in finding more economical and efficient ways of producing wax emulsions.

KEY WORDS: 'WAX'; 'EMULSIFICATION'; 'VARIABLES'; 'MECHANISM'; 'QUALITY'.

DEDICATION.

To my wife Jackie for her patience and understanding.

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1. INTRODUCTION.

1.1. Definition of the Problems.

Wax emulsion products have been a recognised part of the chemical industry for centuries. They regularly occur in such products as polishes and creams for furniture, floors and automobiles; cosmetic and pharmaceutical creams; and are used in various specific industries like printing, paper, fibres and agriculture. A more detailed description of wax emulsion applications is included in Appendix I.

Although the term "emulsion" has many definitions (1), there does not appear to be one comprehensive enough to properly describe the wide range of wax emulsions known to exist. They are manufactured in a variety of physical conditions ranging from thin translucent liquids to almost solid pastes. In common with other emulsions, some products consist of wax particles dispersed in an aqueous medium. These are known as water-out emulsions and they are usually of the non-viscous variety. Others consist of water droplets dispersed in wax and emulsifiers, and are known as oil-out emulsions. It is these latter types which are generally opaque viscous liquids or pastes.

Whatever the particular characteristics of a wax emulsion, it is essentially an intimate mixture of two normally immiscible materials, namely wax and water. The two key materials are persuaded to mix by the addition of surface active agents and usually by the application of physical work.

The combination of wax and water is rarely a permanent one and the so-called stability of the resultant emulsion is a very important factor. This is because wax emulsion products often have to remain effective over months or even years, and separation of the two key constituents would prevent this.

Wax emulsions have been manufactured for a considerable time and the numerous manufacturing techniques are quite well documented. Nevertheless, the results from manufacturing processes can still be unpredictable. Unsatisfactory product can quite regularly be produced requiring at best, labour intensive reprocessing procedures or even a total loss of product. More often than not, the reasons for these occurrences are unknown. From a Quality Control standpoint, the tests conducted on a wax emulsion product are usually orientated towards the physical properties that the finished product must possess. These vary from product to product, but usually measurements are made to assess stability and the disperse phase particle size distribution. There is little doubt that the present methods for the quality control of wax emulsions leave much room for improvement, because the results from stability tests cannot be obtained in time for correction and actual particle size distributions are rarely obtained at all. Even when adverse data is obtained on a particular wax emulsion, a lack of real understanding as to the basic mechanisms of emulsification seems to prevent effective measures being taken to guarantee a more consistent satisfactory product.

1.2. Aims of Study.

From the foregoing discussion, it may be concluded that there are a number of areas of uncertainty connected with the manufacture of wax emulsions. The aim of this study will be to investigate those areas and hopefully gain greater understanding of the various processes and how to assess the results. The specific aims of the study are summarised below:-

(a). To select or devise a satisfactory means for rapidly assessing wax emulsion product quality. In most industries manufacturing wax emulsions, this is currently achieved on a retrospective basis, usually too late to allow the manufacturer any form of corrective action.

(b). To examine the system variables during the wax emulsification process with particular attention to their effects on product quality. Though this has already been attempted to some extent, there appears to have been little progress towards process optimisation. Even the wax suppliers' technical literature appears to give only brief guidance towards successful emulsification.

(c). To investigate the mechanism of wax emulsification in order to have clearer ideas about the type of equipment likely to give best results.

(d). To apply the findings of the study to existing commercial methods and hopefully induce certain processing advantages including reworking substandard emulsions.

1.3. Scope of this Study.

Though the process of wax emulsification essentially involves the combination of wax and water phases, there are several ways in which this can be done. Essentially these may be summarised as follows:-

Atmospheric Processes:-

(a) Molten wax stream added on the water surface.
(b) Molten wax stream added below the water surface.
(c) Water added to molten wax on the surface.
(d) Dissolution of waxes and emulsifiers in solvents then addition to water. This is known as solvent emulsification.

Pressure Method:-

(a) The manufacture of a water in wax emulsion followed by inversion due to further water addition to form a wax in water emulsion.
(b) The direct manufacture of a wax in water emulsion under pressure.
(c) Addition of molten wax to a pressurised water stream via inline blending equipment - as yet unused commercially. Further details are given in Appendix I. The particular method used is usually selected on the basis of the type of wax emulsion required and the manufacturer's equipment limitations.

This study will concern itself with the most widely used European method, namely that of adding molten wax plus emulsifiers to the water surface. The choice of this method has been made for the reasons listed below:-

(a) The method requires fairly simple equipment.

(b) The method of surface addition makes the photography of the process relatively straightforward.

(c) The method is readily controllable.

(d) The method is widely used by wax emulsion manufacturers.

(e) Substandard products are more likely to be made by this method.

2. LITERATURE REVIEW.

The aims of the study have been stated in 1.2 above and the literature review has been divided into four separate sections following those aims. These sections are as follows:-

2.1. Literature on Assessment of Wax Emulsion Quality.

2.2. Literature on Wax Emulsification System Variables.

2.3. Literature on the Theory and Mechanism of Wax Emulsification.

2.4. Literature on Process Developments.

2.1. Literature on Assessment of Wax Emulsion Quality.

The literature available on the subject of emulsions in general is very extensive. However, that part of it dealing with wax emulsions is quite small and largely results from the manufacturers and/or suppliers of waxes. The main objective of this review is to cover literature directly relating to wax emulsions, but due to the sparsity of specific information, some general literature on emulsions has been included when considered relevant.

The most critical property of a finished wax emulsion to any manufacturer is its stability. Wax emulsions are rarely used within a few hours of manufacture and most wax emulsion containing products fail to work in a satisfactory manner when the emulsion shows signs of separation. Therefore, the first part of this Literature Review presented in Section 2.1.1., will be concerned with literature on emulsion stability.

The other criteria of wax emulsion quality are complex and usually related to the finished product application. However, although many varied physical measurements are made, they are usually designed to assess some physical property which may be directly related to the emulsion disperse phase particle size distribution. This is commonly referred to as the emulsion particle size and is generally considered to be one of the most important parameters. Therefore the second part of this literature review, presented in 2.1.2., will deal with methods for particle size analysis.

Although it is recognised that other quality control tests are frequently undertaken, e.g. determination of non-volatiles; percentage light transmission; various viscosity measurements; it is believed that control of emulsion quality is likely to be most successful by measurement of stability and particle size. The argument for the importance of stability determinations has already been outlined and it may be shown that most other emulsion properties are dependant on particle size (e.g. viscosity, translucency or the ability to transmit light). Therefore providing that the quantities and ingredients are correct according to the desired formulation, the control of emulsion particle size and subsequently stability should yield a successful result.

2.1.1. Literature on the Determination of Wax Emulsion Stabilities.

(a) Storage or Ageing Tests.

If a wax emulsion is stable, it will be capable of being stored in its normal container at ambient temperatures for long periods (usually months or years), without separation of wax and water. The simplest and perhaps most traditional stability tests are known as storage, shelf or ageing tests. The test is effected by storing a sample in a suitable container at ambient temperature and observing its change in appearance with time. Typically, within a few hours, creaming or the separation of wax particles onto the sample surface may occur. In a few cases this may be followed by viscosity increase and ultimately perhaps, by the separation of wax and water phases. With most commercial wax emulsions, such changes may take months or even years at ambient temperatures and hence the test gives retrospective information only. Often this information is obtained when it is of little use to the manufacturer.

(b) Accelerated Ageing Tests.

More rapid information can be obtained from accelerated ageing tests when the sample is placed in a suitable container, in turn placed in an oven set at 40 - 60^{o}C, depending on the wax emulsion product. As before, visual changes with time are observed and the time to each change recorded. Levius and Drummond (2) have described the advantages of accelerated ageing tests for pharmaceutical emulsions at temperatures from 4 - 85^{o}C. They proposed that elevated temperatures could be used as an artificial breakdown stress for stability evaluation, but counselled that tests on fine emulsions may prove lengthy.

Levy proved to be a further supporter of the method (3). Details are presented in the American Society for Testing Materials Manual (4) as being suitable for "emulsions". However, most wax emulsions of commercial importance do not give particularly clear results from accelerated ageing tests. After the formation of an initial level of creaming, the wax emulsion usually takes a considerable time to show any further changes. During this study, emulsions have been maintained at 38^{o}C for over a year with little change in their appearance. Therefore though the test is simple to do, it is lengthy and gives retrospective information only, usually relating to creaming rather than phase separation. Though creaming may be important for a particular wax emulsion product, unless it is continuous, it usually represents a gradual separation of incompletely emulsified wax particles. In other words, when considering wax emulsions, creaming is rarely an indication of loss of stability in the sense of phase separation.

Kroner (5) described a stability test based on viscosity measurement via an Ostwald viscometer at 25^{o}C. This test was stated as being used on floor polishes which were based on wax emulsions, by making an initial measurement at 25^{o}C then storing in a sealed bottle at 52^{o}C for 168 hours. A final measurement of viscosity at 25^{o}C completed the test for which he claimed correlations between 168 hours and real storage time in months.

A more recent version of accelerated ageing was described by Appino et al (6), using radio isotopes to label the emulsion disperse phase and subsequently measure rates of separation. Though it is not known if the method could be applied to wax emulsions on a regular basis, it is likely that considerable correlation data would be required with all products before the rapid assessment of stability would be possible. Further, as stated above, many commercial wax emulsions undergo a certain degree of relatively rapid creaming immediately after manufacture. In many cases, after the initial separation of incompletely emulsified wax, the process continues at a very much slower rate.

A further form of accelerated ageing was described by Walker (7). The test was used for synthetic rubbers and samples were subject to freeze/thaw cycling to the point of emulsion breakdown. Fletcher and Mayne (8) also used the method for polyvinyl acetate emulsion paints and it may be that modifications of this technique are applicable to the assessment of wax emulsion stability. The literature contains other papers recording the effects of various emulsions undergoing freeze/thaw phenomena.

Young's paper (9) published in 1934 dealt with the effects of freezing on emulsion structure, and particle coalescence was investigated by Kistler (10) about the same time. Cole et al, (11), investigated the effects of freeze/thaw cycling on butter and other emulsions, and more recent studies on particle coalescence were completed by Pospelova (12), Singleton (13) and Shermann (14). Most of these studies were aimed at describing the physical changes undergone by various emulsions during freezing and no firm conclusions are drawn with respect to using freeze/thaw cycling as a measurement of stability. However, from the above publications, it would seem that the physical changes that may occur during freeze/thaw phenomena, depend largely on the particular emulsion being tested. Therefore correlation data is likely to be required.

(c) Assessment of Emulsion Stability using a Centrifuge.

When an emulsion begins to separate, it usually does so in quite a complex manner (15), being influenced to some extent by external factors such as temperature, density differences between the wax and water, as well as surface forces acting at the wax/water interface. The buoyancy forces are responsible for aggregated or coalesced wax particles migrating to the liquid surface. Similar forces of greater magnitude may be applied to a wax emulsion sample by placing it in a centrifuge and this has been used to measure emulsion stability. Although the literature contains little mention of centrifugal tests for wax emulsions, much work has been done for pharmaceutical emulsions. Becher (1) claimed that centrifugation at 3,750 rpm in a 10cm radius centrifuge for a period of 5 hours, would be equivalent to creaming under the effect of gravity for about 1 year. Further work with a low speed clinical centrifuge at 3,600 rpm was reported by Merrill (15), who related rate of separation to speed. He concluded that a quantitative index of mechanical stability was possible for some pharmaceutical emulsions. However, centrifuging a sample of most wax emulsions currently of commercial interest would merely bring to the surface those particles of partially emulsified wax normally present in an industrial batch.

More recently, the ultra-centrifuge seems to have gained acceptance as a means of measuring emulsion stability. Speeds of up to 50,000 rpm have been reported and emulsion breakdown has been observed both visually and by photography. Again, most of the work in this area has been completed with pharmaceutical emulsions, no mention being made of wax emulsions. Publications giving perhaps the strongest support for this method are those of Garrett (16), and a series of papers by Vold and Groot (17), (18), (19), (20) and by Refeld (21). From their reports it would seem that ultra-centrifugation may be extended to the estimation of wax emulsion stability. The time required to obtain a result can be quite short (less than 1 hour), although longer testing times are needed for fine emulsions. The equipment is somewhat complex and expensive.

(d) Electrical Methods for Determining the Stability of Wax Emulsions.

The stability of any emulsion is largely due to electrical forces at a colloidal level. These electrical forces act at the oil/water interface (24) and are induced or modified by 'emulsifiers'. Several workers have attempted to use electrical measurements to assess emulsion stability. One instrument that has been proved to be applicable to wax emulsions of the oil-out variety is the Fann emulsion tester. This instrument developed by the Fann Instrument Corporation (22) was designed on the principle that an alternating electrical potential tends to break oil-out emulsions. Stability tests may be completed by applying a variable a/c current to approximately 50ml of the sample via two strip electrodes. The voltage imposed across the electrodes is increased until a predetermined amount of current flows. Visual indication of current flow is provided via a flag type galvanometer and relative stability registered as a voltage on a panel meter. During the test, the voltage is raised until movement of the red flag meter occurs at the so-called breakdown voltage. The test is more fully described in Johnson Analytical Methods (23). Unfortunately the instrument is only suitable for oil-out emulsions due to the increased conductivity of the water-out type.

Measurements directly aimed at the electrical double layer surrounding emulsion particles have been made using microelectrophoresis apparatus and the concept of Zeta potential. Becher (1) reports that microelectrophoresis measurements involving the direct measurement of rate of migration of emulsion droplets has not gained wide acceptance because of experimental difficulties. Unfortunately no details are given. However, it is reported that the development of a microelectrophoresis apparatus by Messrs. Zeta-Meter, enable Zeta potential and other measurements to be determined on a sample emulsion within a matter of minutes. Both Becher (1) and Shermann (24) conclude that the measurement of electrophoretic mobilities coupled with particle size determinations should provide a new means of stability determination for emulsions. Further details of the scope of electrophoretic measurements are presented by Overbeek (25). However, it is by no means certain that these type of measurements can be utilised to determine stabilities of wax emulsions. Indeed the complete lack of information with respect to wax emulsions coupled with limited acceptance of the method leads one to conclude that further research is required.

Another electrical method was developed by Kay and Seager (26) which utilised the dielectric properties of emulsions. Once again its development mainly centred around stability determinations on pharmaceutical emulsions of the oil-out type. Claims were made that the method could be extended to water-out emulsions provided that non-ionic emulsifiers were used. The instrument was in commercial production by Messrs. Telray Electronics for a limited period, and has been shown to be successful for oil-out emulsions by S.C. Johnson (23). Unfortunately these same workers found the instrument to be unreliable for all water-out emulsions. As many of the wax emulsions of commercial interest are of the water-out type, this possibly explains why the instrument failed to gain acceptance from the industry.

The electrical method of determining emulsion stability that has probably received the most attention in recent years is that of particle counting. This technique, also reviewed under particle size analysis, is achieved by the 'Coulter Counter' and similar particle counting instruments. These devices cause emulsion particles to pass through a narrow orifice on either side of which is a conductivity electrode. By adding a small quantity of electrolyte to the emulsion, a small current is caused to flow between the electrodes. This current is interrupted each time an emulsion particle passes through the orifice and the resultant pulse registered within the instrument. The size of the pulse is proportional to the size of the particle and hence the distribution is obtained on the measured sample.

However, though the literature contains much information on the use of particle counting as a means of assessing the mechanisms and kinetics by which emulsions either cream, aggregate or coalesce, these works are mostly connected with pharmaceutical emulsions. A summary of the published activities with a Coulter Counter has been prepared by Coulter Electronics Ltd. as recently as July 1974 (27). Though confining itself to those studies made with the Coulter Counter, as this instrument has probably gained the most wide acceptance of its type, the review is quite comprehensive. Many of the theoretical studies have been completed by Higuchi et al, (28) (29). A useful study describing the use of the Coulter Counter for the analysis of oil in water emulsions was completed by Schrenzel (30), during which stability measurements were described on pharmaceutical emulsions. Further studies aimed at investigating aggregation mechanisms in pharmaceutical emulsions and suspensions were completed by Matthews and Rhodes (31).

Once again information appears to be lacking on the use of this technique for assessing the stability of wax emulsions. In fact it may be said that the majority of published work is directed towards understanding the mechanism of emulsion breakdown rather than the assessment of emulsion stability. Computing facilities to process the particle size data often appear to be necessary. The method has been criticised as being insensitive to the small but important changes occurring during the early stages of demulsification (8).

SUMMARY OF FINDINGS FROM THE LITERATURE REVIEW ON THE DETERMINATION OF WAX EMULSION STABILITIES.

(A) There is little information available in the literature that is specific to wax emulsions. The only definite references to wax emulsions are via the methods of accelerated ageing and, via Johnson internal reports, to the Fann Emulsion Tester.

(B) The producers of wax emulsions appear to need a rapid and reliable method for assessing emulsion stability.

(C) Centrifugal and freeze/thaw methods would appear to be the ones most worthy of further investigation on the grounds that relatively simple equipment may be used, yielding rapid results.

2.1.2. Literature on Particle Size Analysis.

(a) Optical Microscopy.

The determination of the particle size distribution of emulsions by microscopic or direct measurement has been widely used. Becher reports it as the method which probably yields the most certain results (1). Usually it is carried out by observing the emulsion under a microscope fitted with a micrometer or graticule eye piece or by using a graduated stage micrometer slide. By tabulation of the numbers of droplets in various size ranges, a distribution curve may be constructed. An early paper by Parsons (32) describes such a method which appears to require much patience.

The addition of a camera to the microscope and the production of photomicrographs allowed a more leisurely examination of the samples. This was described by Becher (1) and the problems of overcoming Brownian movement by using exposures of the order of 1,000th of a second were explained. Refinements on the measurement of droplet sizes from the photomicrographic prints have been carried out by Macklay and Gindler (33) using a special caliper. A more rapid method was produced by Endter and Gebauer (34) using a spot of light made to coincide with the particle by means of an iris diaphragm. The diaphragm in turn was connected to a counting circuit and calibrated to size the particle. By using a battery of counters, both total count and size range were registered and the author reported that a skilled operator could count and size 900 particles in 15 minutes. A similar but less expensive device has been described by Becher (35).

However, although microscopic methods may yield slightly more reliable results (as evidenced by the fact that most other methods are calibrated against microscopy data), even their most sophisticated developments still retain a degree of tedium. This has been reduced by the use of statistical methods resulting in a lower sample count while maintaining small errors with 95% confidence limits (36). No evidence could be found of these methods being used to assess quality of wax emulsions.

(b) Electron Microscopy.

Electron micrographs have been used both to demonstrate the form of various emulsions and to size them. However, the high cost of equipment coupled with some difficulties of sample preparation have generally prevented very much work in this area. S.C. Johnson have produced several internal studies on this subject but they have been aimed at examining emulsion structure rather than sizing particles. Though valuable for theoretical and specific research studies, it is unlikely that such a technique would find very wide application due to the high cost of equipment and the number of skilled man hours involved. Apart from internal Company reports (37), no mention has been found of this technique relating to wax emulsions.

(c) Particle Size Analysis by Light Transmission Techniques.

One of the most widely used techniques for particle size analysis of emulsions has utilised the phenomenon of light transmission. When a beam of light passes through an emulsion, some of the light may be absorbed while part of it is scattered sideways at the surfaces of the dispersed globules. This is because the two intimately combined phases of the emulsion have different refractive indices. Both effects remove energy from a beam of light so that there is a reduction in transmitted light and emulsion particle size data can be derived from either light transmission or light scattering measurements. Measurements based on light transmission or absorption are described as turbidimetry, while those utilising light scattering are called nephelometry.

Turbidimetry.

Walstra (38) (39) developed several techniques involving a U.V. spectrophotometer in order that he could examine emulsions with both small and large particle size distributions. Goulden and Phipps (40) modified the Hilger Bio-chem Absorptiometer by using a combination of filters so that the more expensive U.V. Spectrophotometer could be replaced by a cheaper instrument. Additional work was done by Goulden and Shermann (41). Further developments with a Beckman model D.U. Spectrophotometer were made by Billmeyer and Dezelic (42) (43). However, apart from claims by Dezelic that the above methods yield smaller particle sizes than those obtained by direct microscopic measurement, Slonim et al (44) pointed out that such methods yield only an average particle size and not a size distribution.

The paper of Langlois, Gullberg and Vermulen (45), described an apparatus for the determination of interfacial area in unstable emulsions using light transmission. Unfortunately the examples quoted were rather simple systems and several assumptions were made in order to arrive at particle size distribution data. The authors admitted that further work would be necessary to apply the method to commercial products. However, the use of light transmission for the purpose of the quality control of wax emulsions was described by Queen, Brunson and Johnson (46). Their paper proposed a method using a Beckman D.U. Spectrophotometer or Bausch and Lomb Spectronic 20, to assess wax emulsions by indirectly monitoring particle size. The apparatus was also used to predict properties such as gloss and formulation requirements such as emulsifier levels. Their method involved the dilution of wax emulsions to approximately

1% solids such that the colour factor could be neglected and light transmission be assumed to be a function of particle size only. Though the method is simple to use, an evaluation by S.C. Johnson confirmed that no correlation existed between light transmission and long term stability measured by oven ageing or storage. In addition, one Johnson worker (47) claimed it might be unreliable with commercial products, primarily due to dilution effects (i.e. the possibility of aggregation or coalescence at high dilution). This method is described in Johnson Analytical Methods (23) but has largely been replaced by visual examination. (See Section 4.3.1.).

Light Scattering.

Much of the theoretical work on the phenomenon of light scattering by spherical particles was completed by Rayleigh (48). A light scattering instrument consists of a light source, typically a high pressure mercury vapour lamp which provides a collimated monochromatic beam. This beam is caused to pass through a polariser and hence onto the test cell containing the emulsion sample. The intensity of scattered radiation is measured at various angles with a photo multiplier tube, the output of which is recorded by a highly sensitive galvanometer.

Van der Waarden (49) determined mean diameters of globules in oil water emulsions using a 4358 Angstrom unit mercury line. Wallach et al (50), Gledhill (51), Wales (52), Dettmar et al, (53) have all described techniques of light scattering for the determination of particle size distributions. A more recent study was completed by Weber (54) and both light transmission and scattering received extensive theoretical treatment in the paper of Kerker (55), which also contains an extensive bibliography. No specific reference to wax emulsions has been found.

(d) Holography.

A very recent method combining both light transmission and microscopy was developed by Labrum (56) and Hotham (57). The technique used a pulsed laser light source with a quartz optical system linked to a television camera, a television monitor screen and a video tape recorder. Though this equipment was originally designed to carry out particle size analysis on aerosol sprays, its use has recently been extended to examine wax emulsions by S.C. Johnson (58). The method is still under development, although it is reported that particles from 0.3 microns to 10,000 microns may be analysed. The equipment is very expensive and needs specially trained operators to obtain meaningful results.

(e) Centrifugation and Sedimentometer Techniques.

Generally the disperse phase of an emulsion can be made to separate at an observable rate and the measurement of such rates of separation can provide data for the derivation of a particle size distribution (1). An early apparatus was described by Kraemer and Stamm (59) involving a sample cylinder filled with emulsion and connected to a capillary side arm filled with the continuous phase. As creaming occurred, level changes were observed in the capillary and used to obtain a distribution curve. However, most commercial wax emulsions separate much too slowly for such an apparatus to be of value except as a measure of separation of partially emulsified wax particles.

Separation effects may however be accelerated by centrifugation, and, using similar equipment to that described under stability determinations, particle size data may be generated. Nicholls and Bailey (60) have described a method using an ultra-centrifuge for pharmaceutical emulsions and more recently, Whitby (61), Allen (62) and others have done much to extend the scope of centrifugal sedimentometry. Though excellent results are claimed by Allen (62) making comparisons with microscopic measurements, the apparatus is often complex, expensive and appears to require much operator training to obtain reliable results. In addition, testing times of fine emulsions may be prolonged. There appear to be no examples of the use of this type of instrument for wax emulsions.

(f) Particle Counting Techniques for Wax Emulsion Particle Size Analysis.

Particle counters, of which the Coulter Counter appears to have been the first, if not the most successful commercially, enable large numbers of particles to be analysed semi-automatically with great speed. The Coulter Counter depends upon the principle of drawing a diluted emulsion adjusted with electrolyte, through a small aperture equipped with electrodes.

As each emulsion particle passes through the aperture, it displaces its own volume of electrolyte and imparts momentarily, a usually increased resistance, which is proportional to particle volume. This changing resistance produces a voltage pulse, the magnitude of which also depends on particle volume which is registered in the instrument's counting register. Thus the Coulter Counter records the proportion of particles above a given volume which in turn can be related to particle diameter and subsequently to particle weight.

Though the bibliography on the subject of Coulter counting and particle counting in general is extensive, that which deals either in part or totally with wax emulsions is quite small. The industrial bibliography produced by Coulter Electronics (27) is probably the most extensive and comprehensive document yet produced, dealing with powders, pastes, suspensions and various emulsions. There is an extensive section on pharmaceutical and food products together with various medical uses. However, though numerous oil in water emulsions are cited and some pharmaceutical products that probably contain waxes, no specific mention is made of wax emulsions.

Lien and Phillips (63) published a critical study of the use of a Coulter Counter for oil in water emulsions. They concluded that the instrument had three major problems. These were said to be inaccuracies due to 'noise' (in turn due to electrical and mechanical interferences); a limitation of measureable size range; and the reduction of sample stability due to dilution. The latter problem was considered to be the most serious limitation of the instrument, since dilution factors of over 10,000:- were often required to avoid instrument inaccuracies. Lien and Phillips (63) cited other studies in their paper dealing specifically with the above problems. The paper of Singleton and Brown (64) considered the problems of dilution effects and observed the rapid formation of coalesced or aggregated particles after dilution. Groves (65) looked at ways of retarding this coalescence as did Sprow (66), concluding that various stabilisers could be utilised but the type and quantity for a particular system required trial and error determination. Further studies on emulsions aimed at establishing effects of coalescence with elapsed time were completed by Shotton and Davis (67). These authors obtained their particle size analysis corrected for coalescence by extrapolating to zero time.

Numerous papers appear in the literature on the analysis of Coulter Counter data. Of particular note are the papers of Barnes and Cheng (68), Kellie (69), Shrenzel (70), Short and Rhodes (71) and Marshall (72).

An excellent review article was produced by Matthews (73), with extensive and comprehensive bibliography on the use of particle counters for emulsions and suspensions. He concluded that the Coulter Counter could be used for particle size analysis and for aggregation or de-aggregation studies. Unfortunately no reference was made to the application for wax emulsions. Sherman (24) discussed instrument theory and methods for the analysis of size distribution data. Other particle counting instruments have been described by Particle Data Inc. (74) and Stull (75).

SUMMARY OF THE FINDINGS FROM THE LITERATURE REVIEW ON THE PARTICLE SIZE ANALYSIS OF WAX EMULSIONS.

(A). Apart from the use of light transmission to assess emulsion quality rather than particle size distribution, there is no information available in the literature that is specific to wax emulsions.

(B). Microscopic methods for the particle size analysis of emulsions in general appear to be the most reliable yet the most tedius.

(C). The most rapid methods for particle size analysis of emulsions would appear to be those involving light transmission, which is probably insufficiently accurate, and particle counting which cannot cover the complete particle size range. These methods would also appear to require the least expensive equipment.

(D). It would seem that whatever method for particle size analysis is chosen, considerable work will be required in order to apply it to the analysis of wax emulsions, with no guarantee of success.

2.2. Literature on Wax Emulsification System Variables.

Although waxes have been emulsified commercially for some considerable time, there have been few attempts to analyse the variables of one system. The bulk of the information currently available is either prepared by those companies marketing the various waxes, or results from publications by representatives of those companies.

The most comprehensive technical bulletins on wax emulsification are those issued by Allied Chemical Corporation (76), Hoechst Waxes (77), Eastman (78) and Petrolite Waxes (79). All of these bulletins make brief attempts to highlight the main variables for emulsification together with giving processing methods, brief details of equipment and general informations.

Lange et al, (of Farbwerke Hoechst) (80), (81), (82), published several papers aimed at identifying the system variables during the emulsification of waxes for the manufacture of floor polish. Data was presented showing the effect of changing each variable independently, on percentage floor gloss attainable and emulsion viscosity. A mathematical relationship between the parameters of quality (dry bright effect and emulsion viscosity) was then derived and is illustrated in Table 2.1. This series of papers probably represents the only major attempt to identify the system variables and comment on the relation between them. Unfortunately, Lange's main interest appears to be the statistical method used to obtain the results, rather than effects of the variables.

TABLE 2.1. - DATA OF LANGE et al.

Mathematical connection between influencing and resulting factors

$$\text{Dry-bright effect } R_1 = -892.89+17.822\ J_2\ -0.081126\ J_2^2\ -0.12942\ J_4\ J_6\ -0.12229\ J_4\ J_7$$

$$\text{Viscosity } R_2 = -2.1311\ \frac{-0.09524\ J_1\ J_6}{10^3}\ \frac{-0.57031\ J_2\ J_4}{10^3}\ \frac{+2041\ J_4^2}{10^3}\ \frac{+8.4521\ J_6\ J_7}{10^3}$$

Influencing factors with noticeable influence	Test Range
J_1 = melting time	10 - 30 minutes.
J_2 = wax temperature	80° - 100°C.
J_4 = hardness of water	7.1 - 26.1 dH*
J_6 = cooling period	2 - 8 minutes.
J_7 = emulsifying time	1 - 4 minutes.

Influencing factors without noticeable influence.	Test Range
J_3 = water temperature	80° - 90°C.
J_5 = stirring speed	100 - 1000 rpm.

*dH German unit of hardness.

Von Bramer and McGillen (83) (Eastman Kodak) make brief mention of the system variables for pressure emulsification as being melt temperatures; vessel pressure; emulsifier level; percentage initial water charge; rate of addition of secondary water and rate of cooling. Johnson and Draper (84) (also of Eastman Chemicals) recently produced a concise paper on wax emulsification. This latter paper makes brief mention of the system variables for each emulsification process (water to wax; wax to water; shock cooling; direct saponification and pressure emulsification). Considering wax to water methods, the variables were reported as emulsifier level; wax temperature, water temperature, rate of addition, melt tank size, rate of agitation, and rate of cooling. The importance of the system variables for the emulsification of wax as assessed by various researchers is summarised in Table 2.2. below.

TABLE 2.2.

WAX EMULSIFICATION (SURFACE METHOD). GRADATION OF SYSTEM VARIABLES ACCORDING TO VARIOUS RESEARCHERS

	AUTHORS GRADING OF IMPORTANCE 1 > 10			
VARIABLE	LANGE	HACKETT	JOHNSON & DRAPER	BRIDGWATER & ROBERTS
Emulsifier Level	Not ranked	Not ranked	1	5
Wax Temperature	2	Not ranked	Not ranked	1
Water Temperature	Unimportant	Not ranked	Not ranked	2
Degree of Agitation	Unimportant	Not ranked	Not ranked	3
Wax Addition Rate	5	Not mentioned	Not ranked	4
Rate of Cooling	4	Not ranked	Said to be important	7
Melting Time	1	Said to be important	Not ranked	6
Water Hardness	3	Not ranked	Not ranked	Not ranked

Important information was gathered by Richardson (85) on the actual process of emulsion droplet formation and his paper contained information pointing to emulsion variables.

Rowe (86) examined the effect of emulsifier concentration on the particle size distribution of various mineral oil/water emulsions. He was able to obtain direct relations between emulsifier concentration and the median particle diameter of the resultant emulsion. Other conclusions were drawn for emulsion stability and Rowe demonstrated that there was a minimum concentration of emulsifier for each emulsion, above which his emulsions were stable for two years. Below this level, rapid deterioration was observed. The emulsions were sized with a Coulter Counter.

The effect of perfume constituents of emulsion formulations was reported by Pickthall (87). His paper dealt mostly with cosmetic products, though emulsions containing waxes or waxy products were cited. The author concluded that certain perfumery chemicals (e.g. Hydroxycitronella), could cause a serious loss of stability with certain emulsions.

Roger, Trice and Rushton (88) considered the degree of agitation necessary to produce various emulsions. During this study, the interfacial area of drops formed by shear stresses in turbulent fluid motion was related to the interacted equipment size, turbulence and interfacial tension factors. It was concluded that it should be possible to gather data for the various mass transfer operations occurring during emulsification as a function of fluid mechanics, and relate coefficients determined in small scale experimental units to the coefficients which would form the basis for the design of a large scale industrial plant.

Fondy and Bates (89) investigated the effects of impeller design on the ability to produce stable dispersions using molten metal (Sodium Potassium Alloy) and mineral oil. They concluded that a mean particle diameter is a function of the impeller tip speed and rapidly approaches an ultimate value. They also stated that for minimising power consumption, smaller impellers at high tip speeds were desirable. Though these authors make no mention of wax emulsions, there would appear to be similarity with them. Molten metal can rapidly cool and solidify in a similar manner to wax. That is to say that equipment inducing the formation of a dispersion or emulsion, must in both cases achieve this before a phase change occurs.

A concise review of wax emulsification is given by Hackett with some discussion on the system variables (90). A further paper identifying the system variables is presented in Appendix I. However it would seem that little detailed work has been done in this area for wax emulsions and few general conclusions have been drawn about such systems. Nevertheless, it is most likely that major improvements in process efficiency could be gained from such a study.

SUMMARY OF FINDINGS FROM LITERATURE REVIEW ON WAX EMULSIFICATION SYSTEM VARIABLES.

(A). The already identified system variables are:-

Emulsifier level,
Wax and water temperatures,
Degree of agitation,
Wax addition rate,
Melting time,
Rate of cooling,
Water hardness.

There seems to be some disagreement in the literature with respect to their order of importance.

(B). It is likely that some improvements in wax emulsion product quality could be gained from optimisation of the above variables.

(C). Major processing improvements may be gained from a detailed study of these variables resulting in greater efficiency, reliability and consequently profitability.

2.3. Literature on the Theory and Mechanism of Wax Emulsification.

Although the Greek physician Galen (131 to 201 B.C.) was credited with the discovery of emulsification processes (1), the first attempts to understand the process of emulsification appear to have begun in the 1900's, when Clayton (91) (92) published his initial papers. His excellent reviews of the physical chemistry and chemical engineering aspects of general emulsion formation are largely valid today. In addition, much of the equipment illustrated in his earlier papers is still in use with little modification. However, though a brief study of occurrences at the interface between oil and water was made, and the idea of polar groups mentioned, little detail was given of any likely mechanism of formation.

Further papers on surface activity relating to emulsions followed by Bancroft (93), Lewis (94), and Harkins and Fisher (95). The so called orientated wedge theory is due to Harkins, who postulated that the disperse phase of an emulsion was surrounded by emulsifier molecules suitably aligned to be compatible with the phases concerned. The oil soluble end of an emulsifier molecule was said to align itself with the oil phase and vice versa.

Other early, but notable works on the mechanism of emulsification were those of Stamm and Kraemer (96), Finkle et al., (97) and Thomas (98). All these studies built up the concept of surface activity, the use of emulsifiers, and the way in which they performed, though little mention was made of wax emulsification as a special topic. Apparently it was assumed that wax was really an oil and would emulsify in the same way as other oils. A comprehensive review on the development of emulsion theory is given by Becher (1). A concise review on the theoretical aspects of emulsions was published by Sumner (99), in which he pointed out that there were serious gaps in the emulsion theory which was said to be a mixture of thermodynamics and empirical data. He stated that the three main problems yet to be fully answered were:-

(i). The mechanism by which the emulsifying agent prevents individual droplets from coalescing.

(ii). The mechanism by which the phase relationship in the emulsion is determined.

(iii). The behaviour of an emulsion as a dispersion.

The paper also summarises the work of Bancroft (100), Langmuir and Harkins (101) and others, showing how the concept of surface activity, the orientated wedge theory and the formation of surface films was built up.

Fundamental studies on the formation of emulsion droplets was presented by Richardson using Benzene water emulsions (85). This classical study produced detailed photographs of droplet formation and proposed ways in which droplet size could be related to the physical properties of the system. He concluded that two processes were possible which he called 'injection' and 'turbulent' mixing respectively. Equations relating droplet size to other system parameters were presented.

However, the most relevant information was presented by Hackett (90). He devoted a considerable part of his book to wax emulsification, dealing with the theory of emulsifiers and relating the work of Harkins (95) and Hildebrande (102) to the emulsification of molten waxes. From his book, it would appear that no special mechanisms are considered to operate during the emulsification of waxes that do not otherwise occur during conventional emulsification.

SUMMARY OF THE FINDINGS FROM THE LITERATURE REVIEW ON THE THEORY AND MECHANISM OF WAX EMULSIFICATION.

(A). There is little information to be gained from the literature specifically dealing with the theory and mechanism of wax emulsification.

(B). Literature on the theory of emulsification in general is extensive. The reviews by Sherman (24) and Becher (1) appear to be the most comprehensive, though without mention of wax emulsions.

(C). The published works which actually mention wax emulsions in this respect suggest that existing emulsion theory applies without modification.

2.4. Literature on Process Developments.

2.4.1. General.

It would appear that there is more literature on wax emulsification processes and process developments than on any other branch of this subject. Papers and reviews of general emulsification processes, some of which were applicable to waxes, date back to 1920 when Thomas (98), Stamm and Svedberg (103) and Clayton (92) reviewed ways of making emulsions. Most of these production methods are still in existence today. In fact, it would seem that although emulsion theory has advanced in leaps and bounds, emulsion processing has changed very little. Moreover, although brief reference has been made to a continuous process, there is no evidence that wax emulsification has ever been anything but a batch process.

Publications dealing specifically with processes for the emulsification of waxes appear to date back to the early 1950's with good reviews by Leslie (104), Figliolino (105) and books by Warth (106) and Davidsohn (107). Production methods described in all of these references are very simple, involving melting of the waxes, subsequent addition of emulsifiers, then combination of the two phases at atmospheric pressure.

Jarden (108) briefly refers to processing 'water emulsion waxes', used in floor care. Further details on processing floor care wax emulsions are presented by Sweet (109). He concluded that four methods were available as follows:-

1. Water to wax.
2. Wax to water.
3. Pressure emulsification.
4. Continuous emulsification.

Brunson and Queen (110) of Eastman Chemicals reviewed wax emulsions for floor polishes, suggesting various emulsifiers and process conditions. Further details of emulsification equipment, quality control methods and laboratory emulsification equipment were given by Brunson and Dickert (111).

More generalised and less biased viewpoints of manufacturing techniques and problems were given by Law (112) and Glas, Mahler and Lombard (113). Unfortunately Law's paper lacks equipment details, while the paper of Glas et al., attempts to examine all aspects of emulsification and equipment. Specific techniques and apparatus receive only a brief mention.

However, the major amount of published data specifically dealing with wax emulsions originates from the wax suppliers. Most of the initial "technical bulletins" were from Eastman Chemicals, although all the major wax manufacturers have issued data on emulsification methods and formulae. Bulletins from Allied Chemical (76) and the papers of Lange of Hoechst (80) (81) (82) and Brunson and Queen of Eastman (110) are particularly noteworthy.

Comprehensive summaries of wax emulsification methods are given by Hackett (90), Bridgwater and Roberts (Appendix I) and more recently by Johnson and Draper (84). This latter review is brief, describing typical emulsifiers, formulations, methods of phase combination, and process variables. It confirms the view that apart from pressure emulsification and some innovative work in particle size reduction, manufacturing techniques have made little advance over the past forty years.

2.4.2. Polyethylene Wax Emulsions.

The appearance of polyethylene waxes in the late 1940's seems to have precipitated fresh activity on the processing of wax emulsions. The difficulties were reviewed by McQuillan and Gregg (114) of Allied Chemical. They concluded that most available waxes could be emulsified provided that the correct choice of emulsifier was made. Further processing details were given by Hunsucker (115) who used both wax to water and pressure methods.

Brunson and Queen (110) also discussed the processing of polyethylene waxes admixed with other waxes and highlighted the general need for more elevated melt temperatures. These studies induced the development of pressure emulsification.

2.4.3. Pressure Emulsification of Waxes.

This technique was perhaps first described by Brunson (110) of Eastman Chemicals who certainly did much of the initial work. Eastman claimed that the method was developed almost by accident in answer to a customer query. Initial trials were conducted using a household pressure cooker at 15 p.s.i.g. The development was described by Von Bramer and McGillem (83).

Hunsucker (115) gives more processing information as do the technical bulletins of Allied (76) Hoechst (77) and Eastman (78). Manufacturers have also made improvements to pressure emulsification processes, and the patent of Glaub (116) is a recent example.

2.4.4. Continuous Emulsification of Waxes.

Brunson (111) proposed a method for polyethylene waxes which appears to have been a batch/continuous system, involving a series of melt vessels. Sweet (109) also made brief mention of this technique for polyethylene wax blends. However it is likely that the incumbent difficulties of process control and lack of clear processing advantage are the reasons for its failure to gain acceptance.

2.4.5. Methods for the Size Reduction and Processing of Wax Emulsions.

Peck, Decay and Banker (117) made a comparative study of pharmaceutical emulsification equipment involving particle size reduction of oil and waxy products. They concluded that the Manton Gaulin pump type homogeniser was best suited to these products.

Glas, Mahler and Lombard (113) reviewed particle size reduction equipment for general emulsion manufacture. Though no specific conclusions were drawn, it seemed that these authors were in favour of ultrasonic methods. These techniques were further described by Ashley (118) though only a part of his paper dealt with general emulsification practice.

Both Becher (1) and Sherman (24) give a comprehensive treatment of particle size reduction procedures during the manufacture of general emulsions, concluding that the choice of machine depends upon the product being handled. Comparative work with a guide to equipment selection was completed by Powley (119) and Marshall (120) examined and documented the complete range of emulsification equipment. This latter paper covered equipment from simple propeller mixers, through 'dispersators' and special high shear units to shrouded turbines, pump homogenisers, colloid mills and ultrasonic machines. In addition to an extensive bibliography, notes on equipment selection were included, largely orientated toward product type. No direct mention was made of wax emulsions.

SUMMARY OF FINDINGS FROM THE LITERATURE REVIEW ON PROCESS DEVELOPMENTS.

(A). Basic wax emulsion manufacturing systems were set up in the 1920/30's using batch processing, adding either wax to water or water to wax at atmospheric pressures.

(B). With the exception of the pressure emulsification of wax and the production of emulsions by ultrasonic means, there has been little process development in the production of wax emulsions during the last forty years.

(C). The bulk of the information available on the processing of wax emulsions stems from the wax suppliers.

(D). Much of the process development activity has been directed at pharmaceutical and cosmetic emulsions. Although many of these contain wax or waxy products, the bulk of wax emulsions appear to be used in the polish industry. Equipment in this industry seems to have changed little during the forty years or so covered by this literature review.

3. EXPERIMENTAL WORK PROGRAMME.

3.1. Introduction.

The objectives of the study have already been defined as:-

a. Assessment of product quality.
b. Examination of the system variables during wax emulsification.
c. Investigation of the mechanism.
d. Application of the results to existing processes.

In order to determine the best system for detailed study, it was necessary to carry out a preliminary assessment of some of the key quality parameters. This section will describe this preliminary work and outline the reasons for the particular choice of equipment, formulations and experimental techniques. Sub-sections are therefore presented on emulsification apparatus; formulation selection; techniques for quality assessment; preliminary work on the investigation of system variables; preliminary work on emulsification mechanism and plans for confirmation of laboratory data via pilot plant activities.

3.2. Emulsification Apparatus.

3.2.1. General.

Before any experimental work could begin, a means of manufacturing wax emulsions was required. Reference to

Section 2.2. of this study confirmed that the known process variables were:-

- Emulsifier level.
- Wax Temperature.
- Water Temperature.
- Degree of Agitation.
- Wax Addition Rate.
- Rate of Cooling.
- Melting Time.
- Water Hardness.

Therefore, the experimental apparatus was designed to permit the investigation of at least the above variables. Other considerations with respect to the experimental emulsification apparatus are discussed below:-

(a). Time to Produce a Batch.

Considering the relatively high number of experimental batches likely to be manufactured, the equipment had to be able to produce complete wax emulsions in the shortest possible time. From previous experience and preliminary experiments, this was known to be approximately 30 minutes per batch.

(b). Reproducibility.

The results from experimental batches should be reproducible, which implies the ability to control at least the key variables of the system. Therefore, the experimental apparatus would need the capability to control wax and water temperatures; degree and perhaps type of agitation; wax addition rates; and rate of cooling. The preliminary work indicated that the addition rate of wax to water might be the most difficult variable to control on a small scale.

(c). Cost.

In view of the potentially high cost of some of the ancilliary measuring equipment (for example particle counters), it was decided that the cost of the emulsification equipment and materials should be minimised if possible, as it was anticipated that a relatively large number of batches would need to be manufactured.

(d). Portability.

It was considered essential that the small scale wax emulsification apparatus be portable in order that experiments could be conducted in available and perhaps different laboratory environments.

(e). Availability.

Again in view of the relatively large number of experiments likely to be required, it was considered necessary that the apparatus be totally committed to the project. This was a major factor in constructing a custom made experimental test rig.

3.2.2. Choice of Equipment.

One possibility was to use the wax emulsion pilot plant equipment of Messrs. Johnson Wax Limited. However, this would have necessitated a batch size of 50 gallons, and a batch cycle time of approximately 5 hours. This equipment was rejected for the main programme, on the grounds that it did not satisfy the requirements (a), (d), and (e) above.

Steam heating was rejected for failure to satisfy (a), (c), (d), and (e).

The addition rate of the melted wax was considered the single most difficult variable to control, particularly on a small scale. This was indicated from the preliminary work, where it was found that most wax melts tend to be viscous liquids which readily solidify if cold spots are encountered in valves or transfer lines. From the literature review, it was noted that Hough (121) had found similar difficulties without any apparent solution to them. Initial work with pumps, heated pipe-lines and constant head devices indicated that timed weight addition would probably be most effective on a small scale.

From the above arguments, it was decided that to keep the apparatus as simple as possible. Full details are given in Section 5, although a diagram of the initial design is shown in figure 3.1. below. Electrical heating was chosen using temperature control by rheostat and mercury in glass thermometers. Addition rates were varied by hand pouring, using a stop-clock and electrical balance for check weighing. With practice, it was found that fairly constant rates of addition could be achieved throughout the wax addition cycle. The methods of altering the other variables will be described in Section 5.

3.3. Selection of Formula for Study.

3.3.1. Review of Typical Wax Emulsion Formulations.

Most commercial emulsions contain several other constituents in addition to the wax emulsion. Consultation with the major wax suppliers confirmed the view that the industry manufacturing polishes and creams probably incorporates the largest quantity of wax emulsions in their products, in addition to being one of the largest user of waxes (77). Therefore, the wax emulsion products and intermediates currently made at Johnson Wax were examined because they represented a source of available emulsion data, and because they were typical of emulsions used in a wide range of commercial products. This examination was made in order to produce a relevant but simple formulation for study. The results of this review are presented in Table 3.1., which summarises the emulsion end use; approximate constitution; typical appearance and viscosity; method of manufacture and typical particle diameters as judged via the optical microscope.

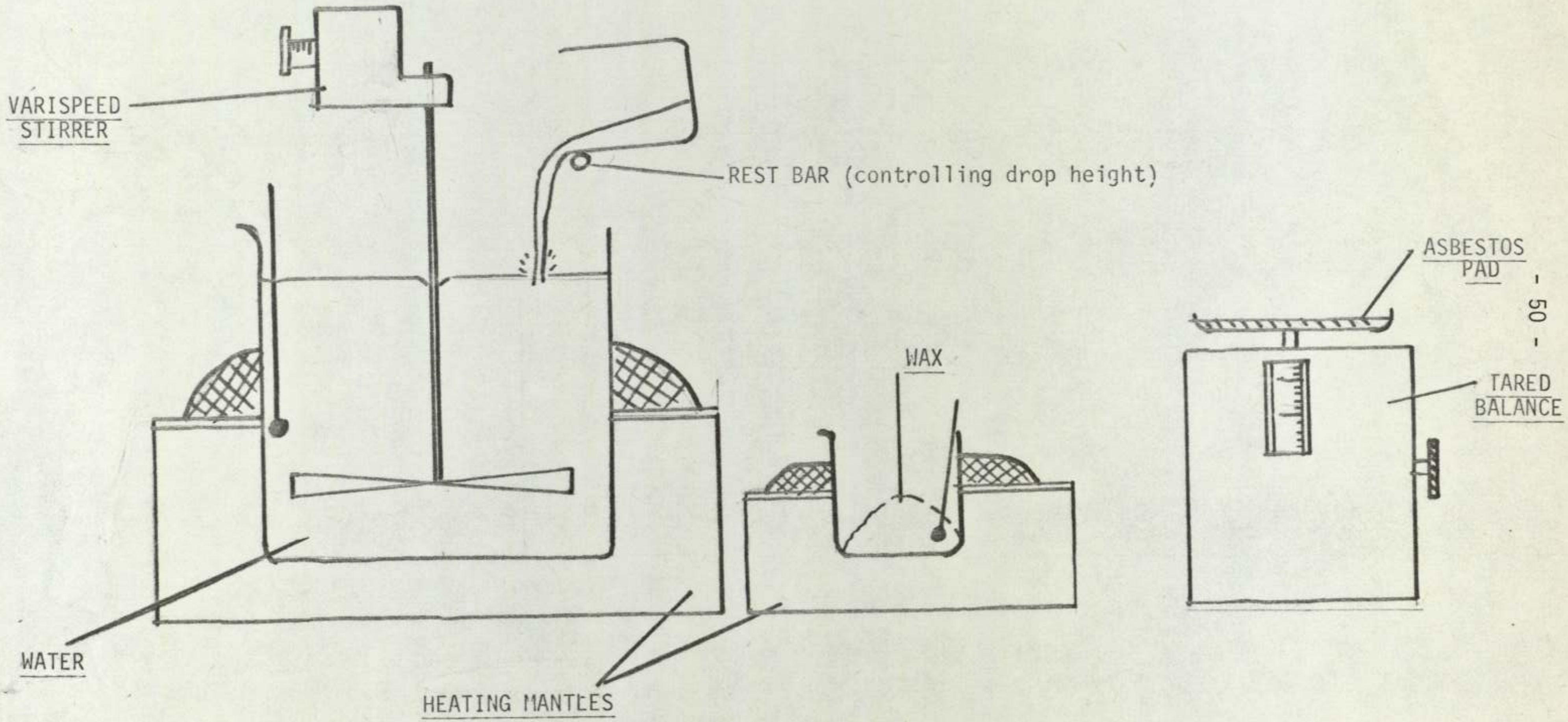
TABLE 3.1. - TYPICAL WAX EMULSION INTERMEDIATES MANUFACTURED BY SPECIALITY CHEMICALS INDUSTRY

CONSTITUENTS % W/W GROUPED BY FUNCTION		TYPE OF PRODUCT				
		SELF POLISHING FLOOR EMULSION INTERMEDIATE	BUFFABLE FLOOR EMULSION INTERMEDIATE	CAR POLISH EMULSION INTERMEDIATE	AEROSOL MULTI SURFACE POLISH INTERMEDIATE	AEROSOL FURNITURE POLISH INTERMEDIATE
a. WAX						
Beeswax						0.25
Carnauba				2.02	1.03	-
Microcrystalline (oxidised)			9.63	0.40		1.36
Paraffin				1.62	0.11	0.09
Reprocessed Montan			3.85	2.70		
Polyethylene		16.59	5.78			
Sub Totals		16.59	19.26	6.74	1.14	1.70
b. EMULSIFIERS						
Fatty Acid)	) Anionic		0.64	1.01		
Amine)	) System		1.49	1.49	0.14	
Alkali)			0.39			
Nonionic)	) Nonionic	3.11			Oil-out 0.71	Oil-out 1.04
Alkali)	) System	0.60			Water-out 0.57	Water-out 0.08
c. PRESERVATIVE.		0.20	0.10	0.42	0.30	0.20
d. DYE.		-	-	-	-	-
e. WATER DILUENT.		78.65	78.13	34.85	68.90	72.07

TABLE 3.1. CONTINUED

CONSTITUENTS % W/W GROUPED BY FUNCTION	TYPE OF PRODUCT				
	SELF POLISHING FLOOR EMULSION INTERMEDIATE	BUFFABLE FLOOR EMULSION INTERMEDIATE	CAR POLISH EMULSION INTERMEDIATE	AEROSOL MULTI SURFACE POLISH INTERMEDIATE	AEROSOL FURNITURE POLISH INTERMEDIATE
f. OTHER ADDITIVES.	Melt viscosity reductant 0.85		Silicones 8.08 Solvents 47.14 Perfume 0.27	Silicones 5.71 Solvents 21.73 Perfume 0.80	Silicones 4.00 Solvents 20.50 Perfume 0.40
Totals	100.00	100.00	100.00	100.00	100.00
g. APPEARANCE.	Translucent water out emulsion.	Slightly translucent off white water out emulsion.	Water out brown opaque emulsion.	Milky opaque water out emulsion.	Milky opaque oil out emulsion.
h. VISCOSITY CENTIPOISE AT 25°C.	5 cps	7 cps	80 cps	15 cps	2000 cps
i. METHOD OF MANUFACTURE.	1. Melt blend wax, emulsifier and Glycol. 2. Saponify with potassium hydroxide at 120°C. 3. Add melt to water at 95°C with vigorous agitation. 4. Cool to less than 30°C.	1. Melt blend waxes and acid at 120°C. 2. Saponify with potassium hydroxide at 120°C. 3. Add amine. 4. Add melt to water at 95°C. 5. Cool to less than 30°C.	1. Melt blend waxes and solvent at 80°C. 2. Charge balance of solvents, acid and perfumes to separate vessel and raise to 80°C. 3. Add 1 to 2. 4. Add amine to water in 3rd vessel and raise to 80°C. 5. Add 4 to 3 i.e. water to wax solution. 6. Cool to less than 30°C.	1. Melt blend waxes, silicones, solvent and oil-out emulsifier then perfume at 80-85°C. 2. Bring water to 80°C add preservative and water-out emulsifier. 3. Add wax to water then amine. 4. Homogenise in pump homogeniser at 3000 psig. 5. Cool to ambient.	1. Melt blend waxes, silicones, emulsifier and part of solvent at 190°C. 2. Preheat balance of solvent to 45°C in 2nd vessel. 3. Add 1 to 2 to give clear solution at 60°C. 4. Add water to step 3 above, giving coarse emulsion at . 5. Add perfume then homogenise via orifice plate at 20-40 psig pressure drop.
j. TYPICAL PARTICLE SIZE (VIA MICROSCOPE) (MICRONS).	Less than 1	1 - 2	5 - 10	1 - 2	40

FIGURE 3.1. - EMULSION APPARATUS (SURFACE METHOD)



From the review and the results presented in Table 3.1., it was decided that the choice should be a wax emulsion typical of those used in floor care products. The reasons for this are summarised below:-

(a) Floor Care Wax Emulsions contain a minimum number of ingredients.

(b) Floor Care Emulsions represent the greatest tonnages produced in the polish industry and are therefore of major importance.

(c) From the experience available from Johnson Wax Limited, floor care wax emulsions are those which give the greatest problems. Therefore, it is likely that if subsequent to the study, improvements in manufacturing techniques could be obtained, the greatest benefit would be felt in this area.

3.3.2. Choice of Wax.

Tables 3.2., 3.3., below show most of the waxes currently in use in the chemical industry (particularly the polish and speciality chemicals industry). They also summarise the extent of usage by Johnson (Table 3.2.) and the major advantages and disadvantages (Table 3.3.).

Preliminary work with naturally occurring waxes such as Carnauba and Beeswax showed that unlike processed natural waxes such as Montan, the quality could be quite variable. Apart from physical form, the colour and quantity of

TABLE 3.2 WAX USAGE IN THE POLISH AND SPECIALITY CHEMICALS INDUSTRY (124)

	TYPE OF WAX	APPROX. COST £/TONNE @ 3/10/77	ANNUAL USAGE BY JOHNSON WAX TONNE	% OF TOTAL WAX USAGE
	PETROLEUM WAXES			
(a)	Paraffins			
	Paraffin 54/57°C	172.00	118.0	29.1
	Paraffin 57/60°C	198.00	1.2	0.3
	Paraffin 60/63°C	187.00	11.0	2.7
	Paraffin 66/69°C	265.00	4.0	1.0
	Sub Total		134.2	33.1
(b)	MICROCRYSTALLINE WAXES			
	Microcrystalline 66/71	299.00	68.1	16.8
	Tan Micro 71/79	369.00	14.0	3.5
	Microx 114	492.00	23.6	5.8
	Microx K30	578.00	16.0	4.0
	Microx K26	610.00	7.0	1.7
	Sasol R.G.	346.00	0.2	0.1
	Sub Total		128.9	31.8
(c)	PROCESSED MINERAL WAXES			
	Hoechst KSL (derived from Montan)	1283.00	1.1	0.3
	Hoechst S (derived from Montan)	1623.00	2.0	0.5
	Sub Total		3.1	0.8
(d)	NATURAL WAXES			
	Filtered Beeswax	1400 - 1800	13.1	3.2
	Carnauba (All Kinds)	1100 - 1400	41.1	10.1
	Ozocerite 525 (Okerin 1980)	492.00	1.1	0.3
	Sub Total		55.3	13.7
(e)	POLYETHYLENES			
	A.C. 6	700.00	12.1	3.0
	A.C. 540	650.00	3.2	0.8
	A.C. 629	650.00	17.0	4.1
	A.C. 680	650.00	51.4	12.7
	Sub Total		83.7	20.6
	TOTAL USAGE/ANNUM (All Grades)		405.2	100.0

TABLE 3.3. - WAXES USED IN CHEMICAL SPECIALITIES AND POLISHES

WAX NAME	MAIN CHARACTERISTICS	MAIN USES	MAIN USES	COUNTRY OF ORIGIN
Paraffin Waxes.	Low cost. Soft to medium wax.	Liquid wax dispersions for wood floors; Paste Waxes.	Melt blended in solvent then cooled.	U.S.A., Europe.
		Auto Polish Emulsions.	Melt blended with solvent, then wax to water followed by homogenisation.	U.S.A., Europe.
		Aerosol Furniture Polish Emulsions.	Melt blended with more expensive natural waxes, silicones and solvents then wax to water to form emulsion. Homogenisation to completion.	U.S.A., Europe.
Microcrystalline Waxes.	Low to medium cost. Hard to medium.	Liquid and paste wax plus autopolish emulsions. Also Aerosol Polishes.	SEE ABOVE.	U.S.A., Europe.
Oxidised Microcrystalline Waxes.	Medium cost. Hard to soft i.e. complete range.	Liquid and Paste wax incl special Cabinet Makers Wax.	Melt blended with other waxes and solvents then cooled.	U.S.A., Europe.
		Also Floor Emulsions.	Melt blended with polyethylene waxes then wax to water emulsification.	U.S.A., Europe.
Processed Montan (Mineral) Waxes.	Medium cost. Usually hard and brittle but range available.	Floor Emulsions (buffable type).	Melt blended with paraffin and polyethylene then wax to water emulsification.	West Germany.
		Auto Polishes and Shampoo's e.g. Wax and Shine type.	SEE ABOVE.	

TABLE 3.3. - WAXES USED IN CHEMICAL SPECIALITIES AND POLISHES CONTINUED

WAX NAME	MAIN CHARACTERISTICS	MAIN USES	MAIN USES	COUNTRY OF ORIGIN
NATURAL WAXES.				
Beeswax.	High cost. Soft Wax.	High quality Cabinet Makers Polish.	See paraffins	China.
		Aerosol Furniture Polish.	See paraffins.	Australia.
Carnauba Wax.	High cost. Hard wax.	Virtually all polishes and creams e.g. Liquid Wax for Wood Floors. Liquid Polish for Furniture. Paste Waxes. Auto Polishes and Shampoo's.	Always melt blended with lower cost waxes, e.g. paraffins, polyethylenes, etc. For liquid and paste waxes, solvent also present then mass poured and cooled. For emulsion polishes, wax and solvent + additives melt blended then added to water. Emulsification usually followed by homogenisation.	S. America. (Brazil).
Ozocerite.	Medium to high price. Hard tough fibrous.	Little used. Mostly for 'Special' Cabinet Maker's Paste Waxes mixed with microcrystalline and paraffin wax.	SEE ABOVE.	E. Europe. U.S.A.
SYNTHETIC WAXES.	Medium cost. Range from fairly hard to soft.	Floor Emulsion polishes usually admixed with Acrylic Polymers.	Often used alone by melt mixing with emulsifier then wax to water emulsification. Also pressure methods.	
			Otherwise melt blended with paraffins or other lower cost waxes then emulsification. Homogenisation rarely used and of doubtful value.	U.S.A. and W. Germany
		Liquid Waxes.	Melt blended with solvents then cooled.	
		Citrus and Fruit Coating Emulsions. Printing and paper emulsions.	Melt blended with paraffins or other waxes then wax to water. Also pressure methods.	

impurities could also vary. Chemical differences were also observed when making a set formulation, such that different batches of these waxes would require different levels of emulsifiers in order to achieve similar emulsion quality. Other waxes are discussed below.

Although from Table 3.2., waxes resulting from petroleum refining represent the largest tonnage used, the paraffins are difficult to emulsify without the presence of another wax. They are rarely used alone.

Microcrystalline waxes are similar to paraffin waxes with the exception of the oxidised type. These tend to be more expensive and rarely used alone.

Processed Montan Waxes emulsify readily but do not possess the required properties for solo use. Melt blending with natural or polythene waxes is most common.

From the data in Tables 3.2. and 3.3., it seemed that Polyethylene and Polyethylene Co-polymer waxes represented a major area of interest for the polish and speciality chemicals industries. These latter materials appear to be available at consistent quality and purity. Based on discussions with the wax suppliers themselves, the only disadvantage of using the polythene waxes appeared to be their direct dependence on oil feed stocks resulting in frequent price increases. However, increased freight and fuel charges coupled with world inflation appeared to induce similar price change frequences with the natural waxes.

An early decision (see Section 1.3.), to confine the study to the atmospheric surface addition method for wax emulsification, necessitated that wax melting ranges needed to be in the low to medium range (85 - 110^{0}C). It was seen that many polyethylene waxes satisfied this requirement.

3.3.3. Choice of Emulsifiers.

Given that a wax emulsion consists of wax, emulsifier(s) and water, it seemed reasonable to choose a system which contained a minimum of constituents and therefore the minimum of formulation variables. Unfortunately, for reasons of product performance, few wax emulsions contain a single wax or a single emulsifier. Emulsifier blends are common as is the use of so-called 'free alkali'.

Continuing the examination of floor care type wax emulsions, (see Section 3.3.), two basic types of emulsifier were seen to be in regular use. From a discussion with the wax suppliers (122)(123),and from the literature survey, it was seen that the more traditional emulsifiers were called 'anionic systems'. These systems consisted of a soap usually formed 'in situ' in the wax melt. The formation of this soap was achieved by the use of an aliphatic fatty acid, usually oleic acid, together with an amine. Common examples of amines were found to be diethylamino ethanol; morpholine and 2 amino-2 methyl-1 propanol (AMP). The systems were termed 'anionic', because solutions of the emulsifier yielded surface active ions with a negative charge. The soap molecule consisted of an oil soluble hydrocarbon chain and a water soluble end to which the amine had coupled. It was reported that amines are usually chosen for use in wax emulsions on the basis of their contribution to the emulsion particle size, colour, raw material cost and volatility (122). For floor care products, it is important that the polish film has resistance to water. After application to the floor, the amine evaporates from the emulsion film so that the water soluble soap tends to revert back to the insoluble water resistant fatty acid. Hence the use of amines with greater volatility usually promotes quicker evaporation, producing a water resistant film in a shorter time. However, an amine with high volatility may be rapidly lost from the wax melt if an open vessel is used. This in turn, leads to an unsatisfactory emulsion due to low levels of emulsifier.

The use of free or fixed alkalies such as potassium hydroxide, was not completely clear. One of the more recent explanations (90) claimed that they were used as a partial replacement for amine in order to reduce cost. Further claims were made concerning the benefit of the alkali when using waxes with low acid or saponification numbers. Again, this was reported to be a question of cost because the more acidic waxes tended to use up amine which, the formulator had destined for combination with fatty acid emulsifier. Though borax had been used, potassium hydroxide at a concentration of 50% w/w seemed to be the preferred alkali for many formulations.

The second type of emulsifier used in floor polish wax emulsions are the "nonionics", which seemed to be gaining increasing popularity. Nonionic emulsifiers do not contain a readily ionisable group and have no electrical charge. They do however exhibit surface active properties and the emulsions prepared with these surfactants are generally stable over a wide range of pH. In addition, they are unaffected by metallic salts and have become very popular for use with metal containing, detergent resistant, ammonia removable emulsion polymers. Some of the most common types of nonionic emulsifiers used with oxidised polyethylene wax are based on ethoxylated nonyl phenols and ethoxylated linear alcohols (usually 12 - 18 carbon atoms per molecule). However, experience had shown that nonionic surfactants did not perform satisfactorily without the addition of a small quantity of free alkali. A recent publication (84) claimed that the reason for the use of free alkali was to neutralise the free acid (presumably from the wax), and saponify ester groups on the wax molecules. Preliminary work indicated that the free alkali was very important to the nonionic emulsifier system, being largely responsible for the control of emulsion particle size and appearance. This work also indicated a finite period of time was required for the saponification reaction to occur. This was contrary to the data issued by some of the wax suppliers (76) (77), which tended to the view that the free alkali need merely be added prior to the addition of wax to water.

Selection of Emulsifier System.

The actual selection of an emulsifier system was largely made on the basis of the trends being adopted by the polish industry. Preliminary work left no doubt that the amine soap emulsifier systems (anionics) required more precise production conditions. Unless sealed wax melt vessels were used, the more volatile amines could easily be lost. When this happened, a poor emulsion resulted due to insufficient emulsifier. Further, most amines seem to be sensitive to light and were liable to change colour on storage, with subsequent colour effects upon finished emulsions.

The nonionic systems on the other hand, were known to be stable even at elevated temperatures and for long periods (120 - 200°C for up to one hour). However, a review of the technical data issued by a major wax supplier (76), seemed to confirm that the nonionic systems had a great dependence on the use of free alkali. Nevertheless, as both emulsifier systems for floor care type emulsions appeared to require its use, a decision was made in favour of the nonionic system for use with polyethylene wax. The Union Carbide product 'Tergitol 15-S-9' was arbitrarily chosen as emulsifier together with 50% by weight Potassium Hydroxide Solution as the alkali.

3.3.4. Choice of Wax Emulsion Formulae.

From the decisions already outlined above, it was concluded that the formula should consist of a single polyethylene wax emulsified by Tergitol 15-S-9 and potassium hydroxide solution. All that remained was to set the quantities for a formula, if possible similar to those of commercial interest. Consultation of the formula file at Johnson Wax produced an emulsion which was a major constituent of a floor care product manufactured throughout the world. Discussions with wax manufacturers indicated that similar emulsions were used by other leading polish manufacturers and therefore the system was of topical interest. A minor disadvantage was that the Johnson Wax emulsion contained one further ingredient, namely ethylene glycol. The reason given for its inclusion in the formula was that it assisted in the reduction of the melt viscosity prior to emulsification. Although this extra additive was contrary to the objectives for a simple formula, it was decided to maintain this choice on the grounds that the formula was of industrial interest. It was thought that the importance of the ethylene glycol additive could be evaluated later. The chosen formula is shown in Table 3.4.

3.4. Techniques for Quality Assessment.

Before the experimental programme to investigate production variables could progress, it was necessary to have a reliable means of judging wax emulsion product. Initially, the quality control methods used by Johnson Wax for wax emulsion products were reviewed and it was found that mostly visual tests were applied (See Section 2.1. and 4.3.1. for further details).

TABLE 3.4.

FORMULATION CHOSEN FOR STUDY

INGREDIENT	PURPOSE	% W/W
AC540 Copolymer	To form emulsion.	16.59
Potassium hydroxide 50% w/w.	To saponify wax and form part of emulsifier system.	0.60
Ethoxylated Linear alcohol (Tergitol 15-S-9)	Emulsifier (nonionic surfactant.	3.11
Ethylene Glycol	To reduce the viscosity of the wax melt.	0.85
Mains water	Diluent.	78.65
Formaldehyde (37% w/w)	Bactericide.	0.20
		100.00

It was concluded that although the tests lacked basic thoroughness, when compared with retrospective information on product stability and general performance, the results were seen to be reliable. Nevertheless, it was felt that for the purpose of this study, at least an evaluation should be made of more detailed and rigorous methods of quality assessment. From the literature review, the choice of quality assessment methods was narrowed down to centrifugal and freeze/thaw methods for stability; and microscopic, light transmission and particle counting techniques for emulsion size measurement. These are discussed in Section 4.

3.5. Investigation of the System Variables.

When a satisfactory means of assessing product quality had been obtained, it was felt that the investigation of the variables associated with wax emulsification should begin. From the literature review detailed in Section 2, many of these variables were already known and summarised in Table 2.2. As stated above, the experimental emulsification apparatus was constructed to allow their measurement and investigation and determine any other factors that influence emulsification. Details of the experimental techniques used and the results obtained are shown in Section 5. Consideration of the known variables suggested that some of them might be interrelated, for example, rate of wax addition and degree of agitation. An initial decision was made to investigate each variable separately, although it was apparent that the experiments might be minimised by investigating several variables simultaneously. It was thought that a final decision could perhaps be made after some initial data had been gathered.

3.6. Experimental Work Leading to a Proposal of Emulsification Mechanism.

As the literature review yielded little definite information on the actual mechanism by which waxes emulsified, it was decided to study the process by means of high-speed photography. A further possibility involving the use of photo micrographs was also considered because of the emulsion particle size ranges known to exist.

The techniques used, the experiments conducted and the results obtained are fully described in Section 6 together with the discussion and conclusions.

3.7. Confirmation of Laboratory Studies via Pilot Plant Work.

Because the study emulsion was chosen to be typical of those of current commercial interest, it seemed reasonable to attempt confirmation of the results obtained on the small scale apparatus via larger scale experiments. Plans were therefore made to produce several batches in the pilot plant 50 gallon reactor and if possible, in the works of Johnson Wax Limited on a 600 gallon scale. The intention was that during these batches, the main conclusions from the study with regard to the process control could be applied and hopefully confirmed. The actual experimental details and results obtained are described in Section 5.

4. ASSESSMENT OF WAX EMULSION QUALITY

4.1. Introduction.

The two basic criteria for assessment of product quality are appearance and performance. Appearance is important mainly from a marketing or consumer viewpoint where the product must meet current aesthetic and similar standards or preferably better them in a competitive situation. Some of the standards of appearance may also to a certain extent, affect performance which can be explained as the ability of the product to do what is claimed for it. Both criteria can often be subjective particularly if the assessment is made by the consumer. In the context of manufacturing a wax emulsion, it is necessary to have some standards for control of both the emulsion as formed and the final product into which the emulsion is incorporated as a minor or major ingredient.

The conventional quality controls include the following tests which are summarised below and explained later in this Section:-

Creaming.

If the product appears to have partially separated on standing to give a cream layer on the product surface, this detracts from its consumer appeal. It also indicates that some of the particles are relatively large, but this is only likely to affect performance if the cream layer cannot be readily reincorporated into the emulsion. For example, the cream layer may dry out and solidify, or the creamer layer particle size may be excessively large (see lumpiness below).

This creaming effect is measured by storage under ambient conditions for long periods, or at elevated temperatures to accelerate the separation effect. Acceleration of the creaming effect under ambient conditions can also be achieved with centrifugation.

Separation.

A badly made wax emulsion will have poor stability characteristics and will tend to substantially separate into an oil layer and a water layer. This will detract from both its appearance and performance.

Measurement is as for creaming.

Lumpiness.

This is related to particle size and the phenomena of creaming and separation. If there are any significantly large particles of say above 500 micron or 0.5mm, these are not only likely to contribute to creaming, but will impair performance by giving an uneven surface to the final dried wax film.

Measurement is by pouring the emulsion down a black glass plate and visual qualitative assessment.

Translucency.

A very translucent product often implies impurity to the consumer and is thus an appearance criterion. It also indicates a small particle size to the manufacturer which may give better performance.

This is assessed visually, and may also be measured qualitatively with a spectrophotometer.

Viscosity.

A relatively viscous product is often more acceptable to the consumer. Viscosity can also indicate the type of emulsion to the manufacturer, and might affect performance.

Measurement is usually qualitative.

Conventional quality control is thus based on a combination of qualitative assessments and storage tests which either take too long to be effective as in the case of ambient and accelerated storage tests, or are unquantified and/or subjective as transluence or lumpiness testing. All the current test methods outlined above either measure stability or give an indication of particle size.

The property of any wax emulsion probably of foremost importance to a manufacturer, is its stability. Few wax emulsions are used within a short time of manufacture and are required to be stored for long periods of up to 2 years under a variety of conditions ranging from near freezing to tropical temperatures. Even though a particular product may contain only a small percentage of wax emulsion, the separation of this constituent is virtually certain to reduce product performance and drastically impair product appearance.

The importance of emulsion particle size is sometimes less apparent. Nevertheless, the size of the wax particle directly affects most of the important properties of an emulsion. Large particles can lead to creaming as described above. During this process these large particles migrate to the emulsion surface often forming a thick wax layer. Particle size has fairly major affects on other physical properties such as viscosity and emulsion type. The type of film laid down by the finished product can also be adversely affected by coarse wax particles. However, it is probable that because of the experimental difficulties involved, the measurement of wax emulsion particle size is rarely attempted directly for quality assessment purposes. Often some parameters are measured which may be related to particle size, for example, percentage light transmission. Whatever the means used, particle size would appear to be the second major control criterion for quality assessment.

Although other criteria for quality assessment were encountered via previous experience and from the literature review in Section 2, it was decided that an investigation of stability and particle size methods would cover all these other methods because of the interrelationships known to exist. A further conclusion was that if a stable wax emulsion could be produced, it was generally satisfactory for its particular function. Hence wax emulsion performance can largely be attributed to stability and therefore this parameter may be measured to assess 'performance'. Similarly, particle size measurements were seen to be the best way to assess emulsion appearance.

4.2. Main Conclusions from the Literature Review.

4.2.1. Stability Measurement.

The literature review and previous knowledge of the polish industry led to the conclusion that methods involving centrifugation and freeze/thaw cycling were likely to prove most worthy of further investigation. Therefore, these were selected for study, and the results compared to conventional testing methods.

4.2.2. Particle Size Analysis.

Particle size analysis of traditional emulsions has been tried via a variety of methods. It would seem however, from Section 2, that the methods which are most likely to be applicable to wax emulsions are those of microscopic analysis; light transmission analysis; and particle counting. Moreover, only one of these techniques has been used specifically for wax emulsions, namely that of light transmission. It was therefore decided to review this method first but also to evaluate the other methods.

4.3. Existing Methods for Quality Assessment by Evaluation of Performance and Appearance.

4.3.1. Existing Quality Control Tests on Wax Emulsion Intermediates.

The quality control methods used by the company for wax emulsions were first reviewed. This examination revealed that apart from some experimental studies with light transmission (see Section 2), the methods used were very simple and straight forward. Typically for a wax emulsion intermediate destined for a floor polish, the emulsion type would just be ascertained by taking a small sample of the emulsion and testing it's miscibility with water. Complete miscibility with water would indicate a water-out emulsion (usually the type required), and immiscibility an oil-out emulsion.

Assuming a water out emulsion were found, light translucency would then be examined by slowly pouring approximately 10 millilitres of product from one receptacle into another. Visual examination of the transferring liquid would subjectively assess (translucency) or opacity. In general, a high degree of translucency would indicate a product which should meet both performance and appearance objectives.

In addition, a non-volatile or solids content of the emulsion would be completed by placing a weighed sample in an oven at 145^{o}C, for a fixed period of time and re-weighing. This would determine if the concentration of waxes was at the desired level and, if necessary, the appropriate adjustment of water could be made.

Other tests might include pouring the emulsion on a highly polished black glass plate and examining the dried film for visible agglomerates, i.e. assessing 'lumpiness'. Again, this test evaluates both performance and appearance characteristics. The presence of a large number of visible particles on the plate would suggest that the product may perform badly and cream within a short time of manufacture. These results would be correlated with the transparency test described above.

Assuming that the wax emulsion intermediate satisfied the above tests, it would be used to make the final product.

An oil out emulsion would be subjected to a microscopic examination and possibly its viscosity determined in addition to the solids content.

4.3.2. Existing Retrospective Testing on Finished Products.

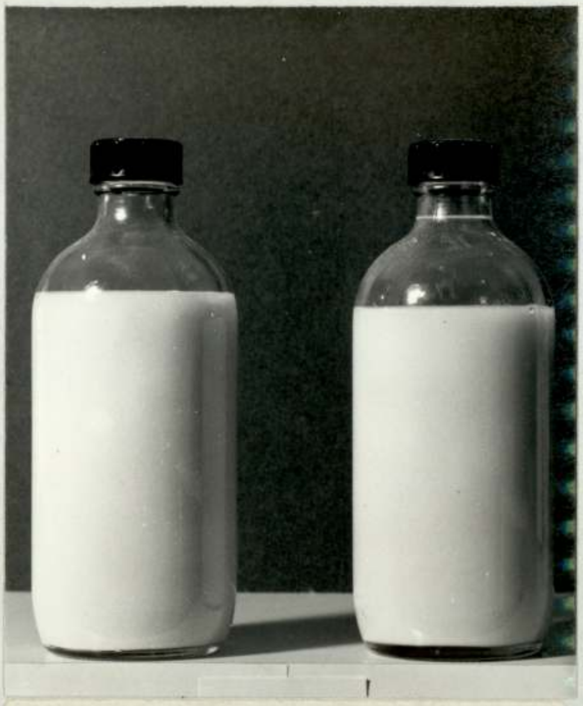
A number of tests are carried out on finished products containing wax emulsions as an ingredient. As explained in Section 4.1. above, these tests relate to both appearance and performance, and are described in more detail below with some typical results.

(a). Ambient Storage.

Ambient Storage Tests are usually conducted in 250ml sealed glass bottles, when samples are held usually for at least one year. During this time, visual changes that occur are recorded, together with the lapsed time when they occurred. A review of quality control records confirmed the view that in the majority of cases, meaningful data was only obtained after several months. The main disadvantage of this method is therefore the time needed to obtain a result which ideally requires lengthy storage of product before distribution which is not practical. Typical results are shown in Plates 4.1. to 4.4. and in tabular form in Table 4.1.

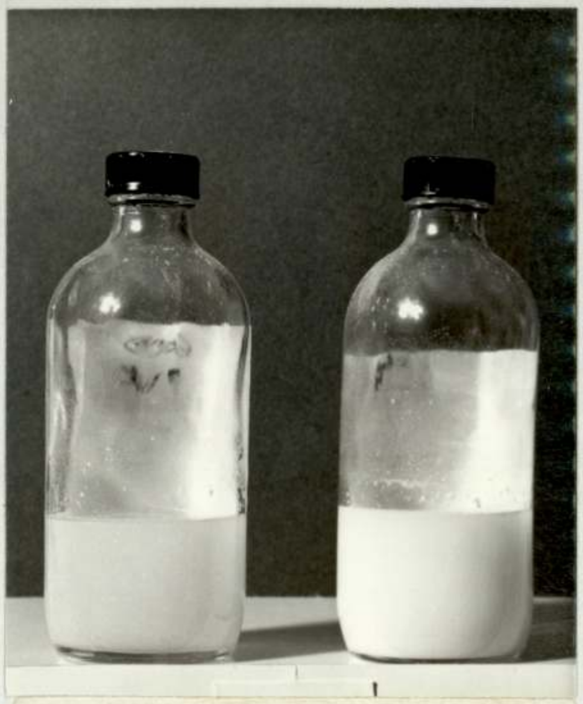
(b). Accelerated Storage.

The Accelerated Storage Tests were initially considered to be more likely to be useful. This test is normally conducted by taking 25ml sample in sealed glass bottle and storing it in a forced draught oven set at 60^{o}C. As for (a) above, the sample is examined periodically, when the visual changes and lapsed time are recorded. A review of Johnson Wax Quality Control records for wax emulsion products showed that again, in the majority of cases, quite long periods (i.e. at least several weeks) were required for changes in appearance to occur. Typical data for several wax emulsion products is presented in Table 4.2. below. Visual changes normally encountered with this type of test are illustrated in Plates 4.5. to 4.8. The results of preliminary experiments



A - PLATE 4.1. - GOOD PRODUCT - B
(AMBIENT STORAGE)

A - PLATE 4.2. - BAD PRODUCT - B
(AMBIENT STORAGE)



A - PLATE 4.3. - GOOD EMULSION - B
(AMBIENT STORAGE)

A - PLATE 4.4. - BAD EMULSION - B
(AMBIENT STORAGE)

AMBIENT STORAGE

A - as made
B - after 12 months

TABLE 4.1. - AMBIENT STORAGE (AGEING TESTS)

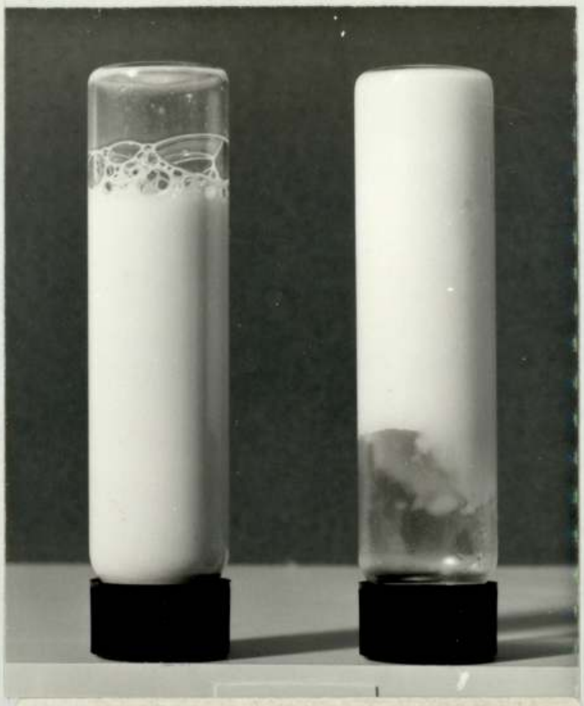
SAMPLE BATCH NUMBER	APPEARANCE AFTER STATED PERIOD							COMMENTS
	24 HOURS	168 HOURS (1 week)	336 HOURS (2 weeks)	730 HOURS (1 month)	2190 HOURS (3 months)	4380 HOURS (6 months)	8760 HOURS (1 year)	
1	No cream. Translucent emulsion.	No change.	No change.	No change.	No change.	1mm cream.	No change.	Standard formula for study emulsion.
2	½mm cream. Translucent.	No change.	No change.	No change.	No change.	1mm cream.	No change.	Standard formula for study emulsion.
3	Opaque emulsion. Some free wax 15mm cream.	Opaque emulsion. 30mm cream.	Cream coalesced and dried forming solid layer.	No change.	No change.	No change.	Complete solid skin 25mm thick. Over surface of emulsion.	50% of formula weight of nonionic emulsifier.
4	Opaque emulsion 13mm cream.	Opaque emulsion. 40mm cream.	No change.	40mm solid cream layer. Translucent emulsion beneath.	No change.	44 mm solid cream layer	Complete solid skin 45mm thick. Emulsion stable.	50% of formula weight of nonionic emulsifier.
5	Opaque emulsion much solid wax. 40 mm cream.	40mm of cream and solid wax.	Sign of separation.	Complete separation.	No change.	No change.	No change.	10% of formula weight of KOH.
6	Opaque emulsion some free wax. 50 mm cream.	Free wax and 50 mm cream.	Opaque emulsion.	Separation occurring.	Complete separation.	No change.	No change.	10% of formula weight of KOH.
7	Very translucent emulsion. No cream.	No change.	No change.	Slight viscosity increase.	Further viscosity increase.	No change.	No change.	150% of formula weight of KOH.
8	Very translucent emulsion. No cream.	No change.	No change.	Slight viscosity increase.	Further viscosity increase.	Gelled.	No change.	150% of formula weight of KOH.
9	1mm cream. Translucent.	No change.	No change.	Slight colour change.	No change.	No change.	No change.	Standard works batch of buffable floor emulsion intermediate for study emulsion.
10	Translucent emulsion. No cream.	0.5mm cream.	No change.	No change.	No change.	Slight viscosity increase.	No change.	Standard works batch of drybright emulsion intermediate for study emulsion.

TABLE 4.2. - TYPICAL ACCELERATED STORAGE DATA FOR WAX EMULSION CONTAINING PRODUCTS

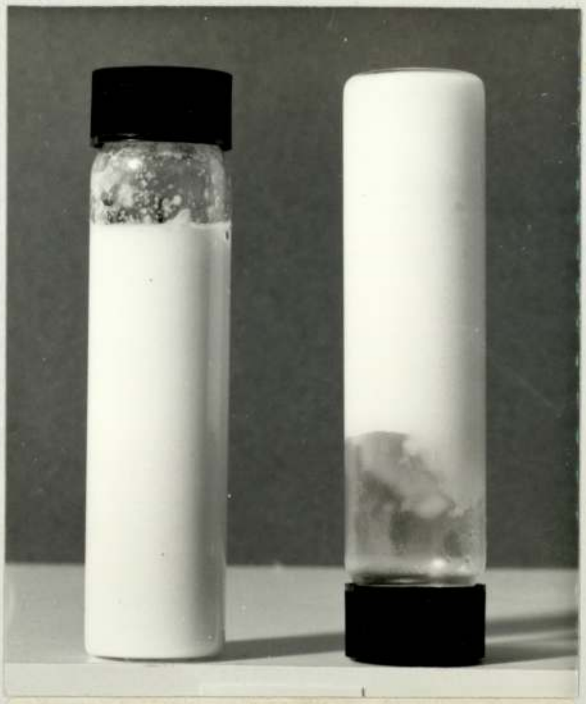
(STORAGE TEMPERATURE = 60^{0}C)

PRODUCT TYPE	BUFFABLE FLOOR POLISH	SELF POLISHING OR DRYBRIGHT FLOOR POLISH	NEW ALL POLYMER FLOOR POLISH	BUFFABLE CAR POLISH	INTERMEDIATE FOR AEROSOL FURNITURE POLISH
% Wax Emulsion	56.0	8.5	NIL	85.1	100
Visual examination after stated period.					
1 day (24 Hours)	No change.	No change.	No change.	Slight* spirit separation.	10% spirit* separation.
1 week (168 Hours)	Slight sediment.	Some slight sediment.	No change.	Slight spirit and 1% water separation.	25% spirit* separation. 1% water separation.
2 weeks (336 Hours)	Slight sediment.	Some sediment.	No change.	No change.	No change.
1 month (730 Hours)	Viscosity increase.	Some sediment.	Slightly cloudy.	No change.	No change.
3 months (2190 Hours)	Gelled.	Viscosity increase.	Slightly cloudy.	Gelled.	25% spirit separation* 5% water separation.
6 months (4380 Hours)	Gelled.	Further viscosity increase.	Cloudy and yellow.	Gelled.	No change.
12 months (8760 Hours)	Gelled.	Gelled.	Gelled	Gelled.	Gelled.

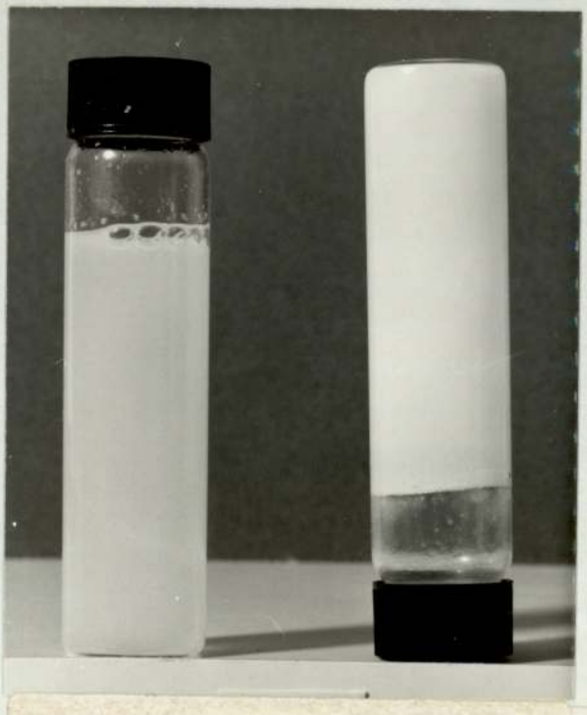
*Some products contain white spirit.



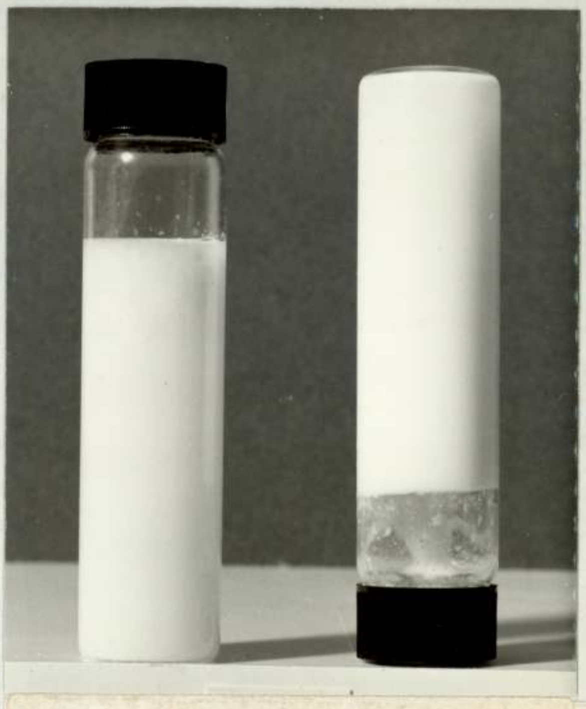
A - PLATE 4.5. GOOD PRODUCT - B
(ACCELERATED STORAGE)



A - PLATE 4.6. BAD PRODUCT - B
(ACCELERATED STORAGE)



A - PLATE 4.7.GOOD WAX EMULSION - B
(ACCELERATED STORAGE)



A - PLATE 4.8.BAD WAX EMULSION - B
(ACCELERATED STORAGE)

ACCELERATED STORAGE TEST @ 60°C

A - as made
B - after 3 months

with the study emulsion are shown in Table 4.3.

As may be seen from Table 4.2. several months are often required before any major changes are apparent with finished products. By using this technique, it was hoped that with basic wax emulsions, results would occur more quickly. As seen from Table 4.3., this was rarely the case.

When it was apparent from the results of trial storage tests, (both accelerated and at ambient temperatures), that in most cases only information on the rates and extent of creaming could be obtained, other methods were attempted.

4.4. Techniques for the Assessment of Wax Emulsion Appearance Investigated and Developed during this Study.

The arguments for attempting to measure emulsion particle size in order to quantitatively assess appearance have already been outlined in the introduction to this section (See 4.1.). It was further decided via the literature review that the size measurement methods most likely to be adaptable to wax emulsions were as follows:-

(i) Microscopic Analysis.
(ii) Light Transmission Methods.
(iii) Particle Counting Techniques.

The literature review provided further information on the above techniques (summarised in Table 4.4.), which indicated

TABLE 4.3. ACCELERATED STORAGE (AGEING) TESTS @ 60°C ON WAX EMULSION

SAMPLE REFERENCE	APPEARANCE AFTER STATED PERIOD							COMMENTS
	24 HOURS	168 HOURS	336 HOURS	730 HOURS (1 month)	2190 HOURS (3 months)	4380 HOURS (6 months)	8760 HOURS (1 year)	
Batch 1	1mm cream Translucent emulsion.	No change.	No change.	Slight darkening in colour.	Slight viscosity increase.	Slight viscosity increase.	No change.	Standard formula.
Batch 2	No cream. Translucent emulsion.	No change.	No change.	No change.	No change.	No change.	No change.	Standard formula.
Batch 3	Opaque emulsion. 3mm cream and free wax.	No change except slight darkening in colour.	No change.	No change.	No change.	No change.	Cream now solid layer.	50% of formula weight of nonionic emulsifier.
Batch 4	Opaque emulsion. 5mm cream and free wax.	No change except slight darkening in colour.	No change.	No change.	No change.	No change.	Cream now solid layer. Stable emulsion beneath.	50% of formula weight of nonionic emulsifier.
Batch 5	Opaque emulsion. Free wax and cream. 4mm on surface.	Complete separation.	No change.	No change.	No change.	No change.	No change.	Standard formula with 10% of formula weight of KOH.
Batch 6	Opaque emulsion. Free wax and cream. 4mm on surface.	Signs of separation i.e. translucent liquid at base of bottle.	Complete separation	No change.	No change.	No change.	No change.	Standard formula with 10% of formula weight of KOH.
Batch 7	Very transparent emulsion. No cream.	Viscosity increase.	Gelled.	No change.	No change.	No change.	No change.	150% of formula weight of KOH.
Batch 8	Very transparent emulsion. No cream.	Viscosity increase.	Gelled.	No change.	No change.	No change.	No change.	150% of formula weight of KOH.
Batch 9	1mm cream. Translucent.	No change.	No change.	No change.	No change.	No change.	Slight darkening of colour.	Standard works batch of buffable floor emulsion intermediate.
Batch 10	Translucent. No cream.	No change.	No change.	No change.	No change.	No change.	No change.	Standard works batch of buffable floor emulsion intermediate.

TABLE 4.4. - LITERATURE SURVEY OF TECHNIQUES FOR PARTICLE SIZE ANALYSIS

METHOD	ADVANTAGES	DISADVANTAGES	CONCLUSIONS WITH REGARD TO STUDY
Microscopic Analysis			
(a). Optical	Can be very accurate and provide permanent record via photomicrographs. Often used as primary standard for other methods. Relatively easy to use.	Relatively high cost of equipment. Particle counting can be very slow and tedious. Analysis below 1 micron impossible.	Optical microscope with camera available. Study should investigate if rapid comparative method possible. Test first.
(b). Electron	Accurate. Permanent record possible. Lower size limit likely to incorporate all particles in the emulsion range.	High cost equipment. Skilled operators required. Sample preparation difficult.	Equipment not available and might be very time consuming to use. Reject for this study.
Light Transmission Measurements			
(a). Light scattering.	In the context of wax emulsion, none worthy of mention.	Equipment not available for this study. Computation of particle size complex. No reference found on wax emulsions.	Reject for this study.
(b). Light Transmission.	Low cost equipment. Rapid and easy to use. Already cited in literature as being suitable for wax emulsions. Available for this study.	No particle size analysis given. Accuracy of results questionable due to colour effects and possibility that particles not all spherical.	Evaluate for the quality assessment of wax emulsions. Test second.

TABLE 4.4. CONTINUED - LITERATURE SURVEY OF TECHNIQUES FOR PARTICLE SIZE ANALYSIS

METHOD	ADVANTAGES	DISADVANTAGES	CONCLUSIONS WITH REGARD TO STUDY
Electronic			
Particle Counting	Rapid and easy method. Lower limit equal to that of optical microscope. Medium cost equipment available for this study. Particle size distribution possible.	No definite evidence of being satisfactory for wax emulsion. Electrolyte has to be added to emulsion before measurements taken. Measurements taken at high dilution with attendent possibility of changing product.	Evaluate the suitability of use with wax emulsions. Test Third.
Sedimentation Methods			
(a). Centrifugal photosedimentometry	a). Very accurate. Wide size range possible. Particle size distribution possible. Permanent record possible.	High cost of equipment. Skilled operators required. Equipment not available for this study. Somewhat time consuming.	Reject for this study.
(b). Other methods	b). High accuracy.	Too slow	

that microscopic methods should be tried first followed by light transmission and then particle counting.

4.4.1. The Assessment of Wax Emulsion Appearance by Microscopic Analysis.

(a). Apparatus.

A Vickers M17 model optical microscope equipped with 4x; 10x and 40x objective and a 12.5x eyepiece was used incorporating an oil immersion objective (100x) and an integrated 35mm camera body and extension tube. Large slides (30mm x 60mm) were used in conjunction with standard coverslips. Kodak HP5 fine grain film at 400 ASA was used with a 1mm stage micrometer scale graduated in 2 micron divisions.

(b). Technique.

In order to minimise contamination from airborne dust and general dirt, the microscope was mounted in a special clean room normally reserved for optical (analytical) instruments. The microscope optics were regularly cleaned prior to use with special lens tissues supplied by the manufacturer and it was kept covered when not in use.

All glassware was rinsed with water then acetone and allowed to dry in a laboratory oven. Before use, glassware was lightly wiped with a lens tissue moistened with filtered alcohol. During use, glassware was handled with laboratory tweezers to avoid grease pick-up from the hands. Alternatively, disposable polythene gloves were worn.

Samples were prepared by first shaking the sample bottle then withdrawing the aliquot to be analysed on a solid glass rod. The sample was then transferred to the slide by either gently shaking the rod when positioned over the slide or gently touching the slide. A coverslip was then gently but squarely dropped into place such that most of the air was excluded. Excess product was removed from the coverslip edges with an absorbent tissue. The sample was then transferred to the microscope stage and viewing and photography effected according to the manufacturers instruction booklet (124). The degree of magnification utilised depended on the product being examined and the type of information required. However, it was found that with the study emulsion, a substantial part of the wax was present as particles at or below 1 micron in diameter. Consequently, it was impossible to obtain a particle size distribution by measuring and counting, as particles below about 0.5 micron cannot be distinguished with an optical instrument (1). Nevertheless, a qualitative analysis was able to be carried out with all batches of the study emulsion, identifying particles which were likely to cause creaming or idicate instability. (See Table 7.2.). In addition, the microscopic analysis method was made partially quantitative by the modification discussed below.

A high quality standard sample of the study emulsion was prepared using the standard formula and process conditions.

This was photographed at 500x magnification and printed on a 13cm by 9cm format. Using a transparent overlay of a scale in microns, (traced from a photomicrograph of the stage vernier at 500x magnification), the number of particles greater than an arbitrary 10 microns was determined. This figure is explained and justified later. The process was repeated over three batches and the three results were averaged to give a value of 3 which was taken as a standard level of particulates greater than 10 microns. This value was used as a basis for ranking all other emulsions by defining and emulsion creaming number as:

$$\text{Emulsion creaming number} = \frac{\text{Number of particles greater than 10 micron on a 13cm x 9cm format}}{3}$$

The above method was supplemented with the photomicrographs of emulsions to be analysed, enabling comparisons to be made and the faults identified. The microscopic method was thus developed as a primary source of reference on emulsion quality and to assess creaming tendency.

(c). Results.

Plates 4.9. - 4.16. show batches 1 to 8 at 500x magnification. Plate 4.17. shows the stage vernier at 500x magnification from which the overlay for creaming number was made. Table 4.5. presents the results for creaming number for batches 1 to 8 and compares these results with

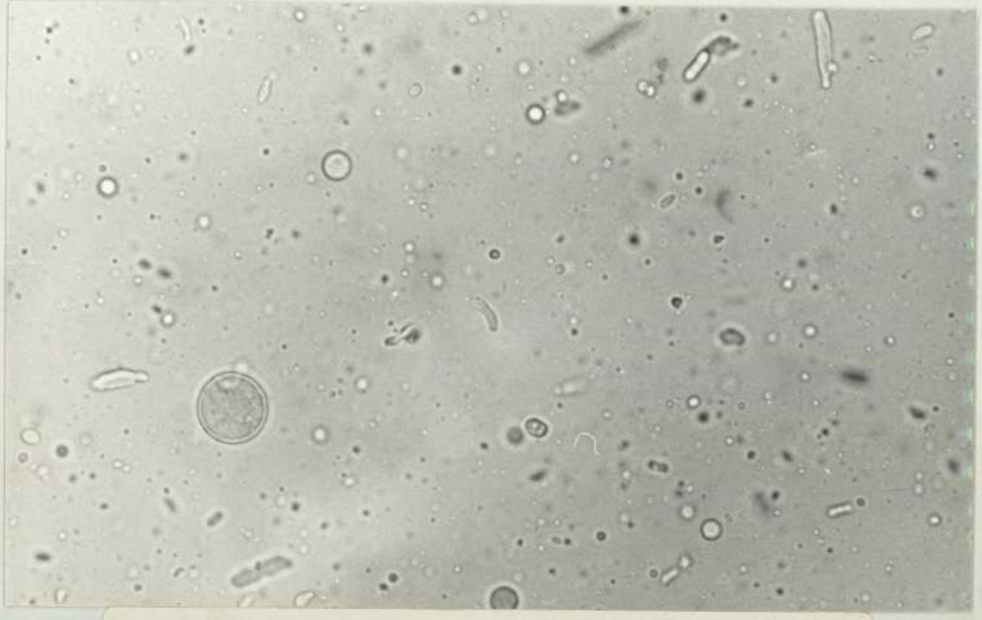


PLATE 4.9. BATCH 1 - GOOD EMULSION
500 x MAGNIFICATION

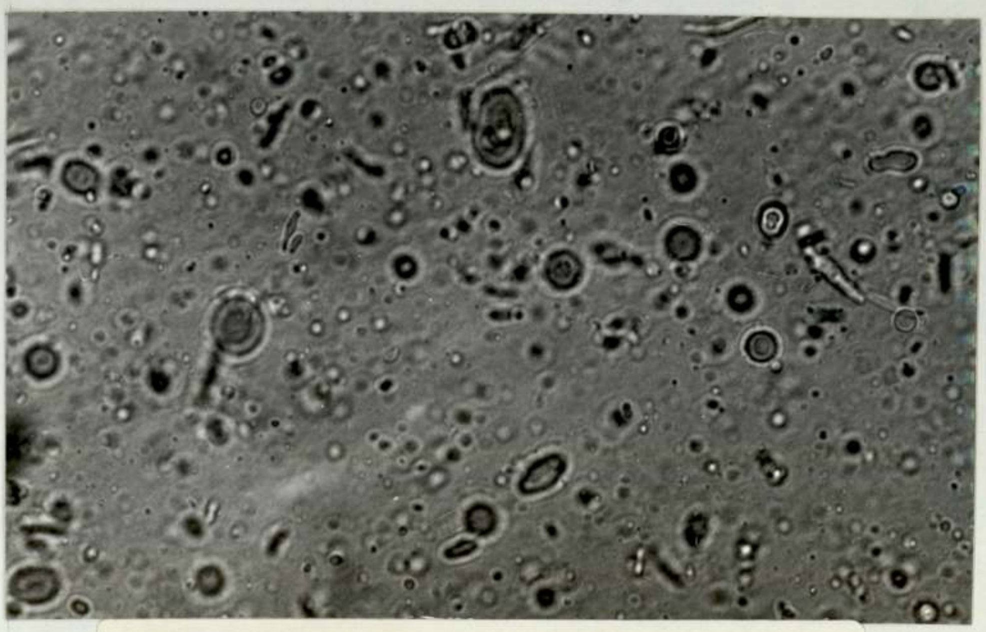


PLATE 4.10. BATCH 2 - GOOD EMULSION
500 x MAGNIFICATION

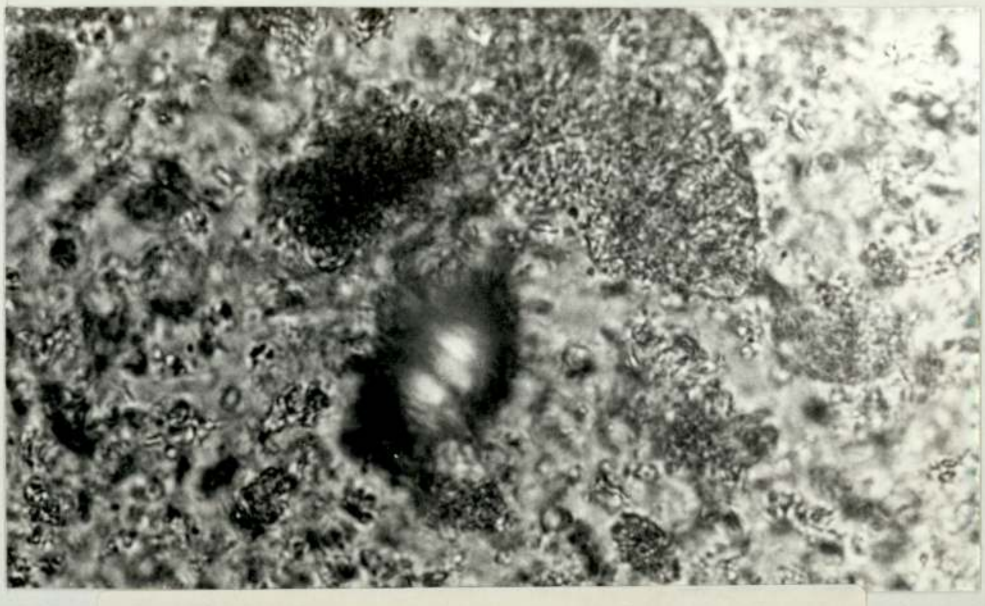


PLATE 4.11. BATCH 3
MADE WITH REDUCED EMULSIFIER
500 x MAGNIFICATION

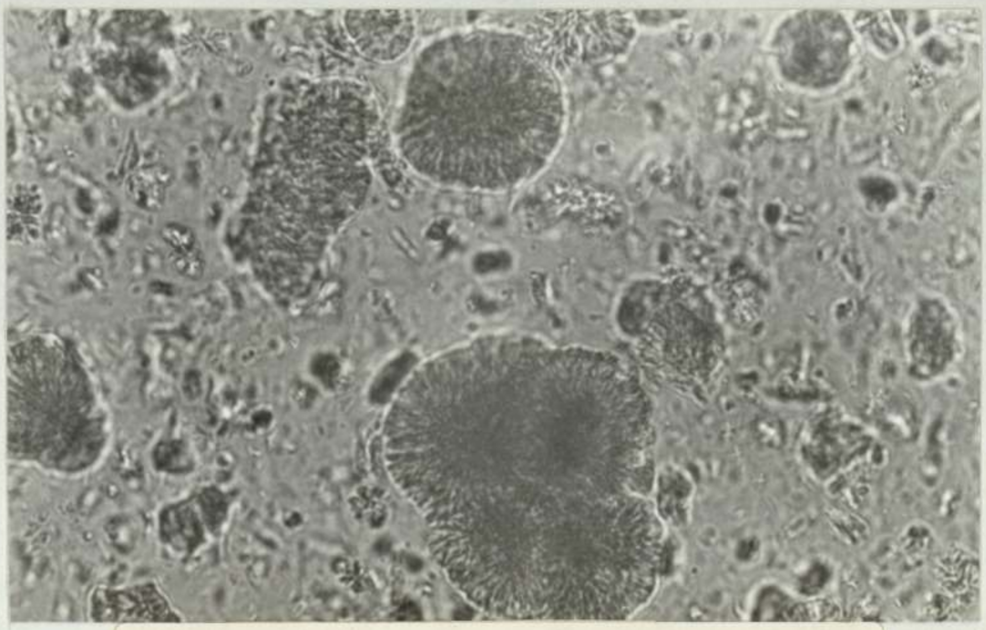


PLATE 4.12. BATCH 4
MADE WITH REDUCED EMULSIFIER
500 x MAGNIFICATION

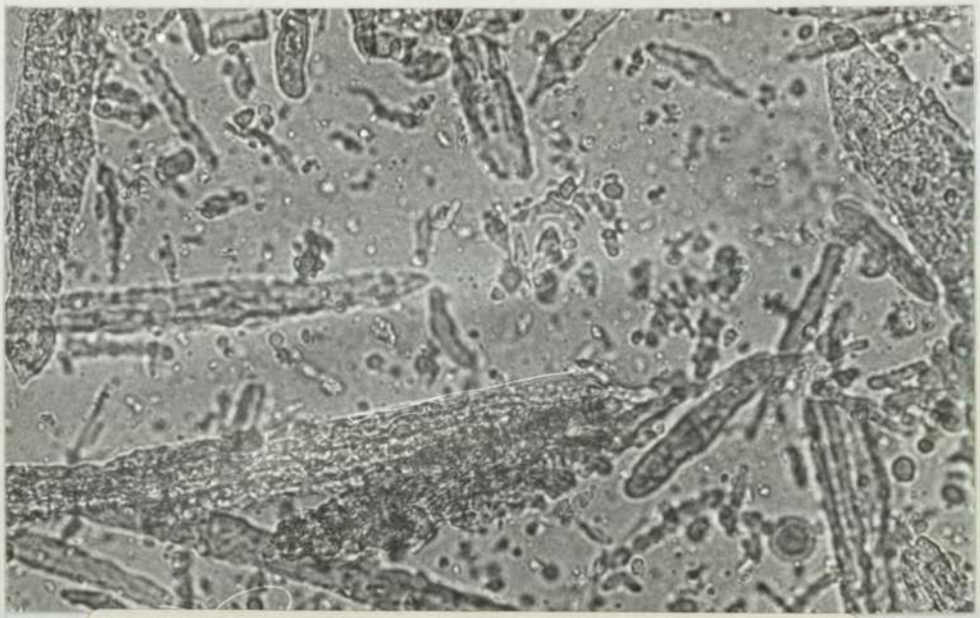


PLATE 4.13. BATCH 5
MADE WITH REDUCED ALKALI
500 x MAGNIFICATION

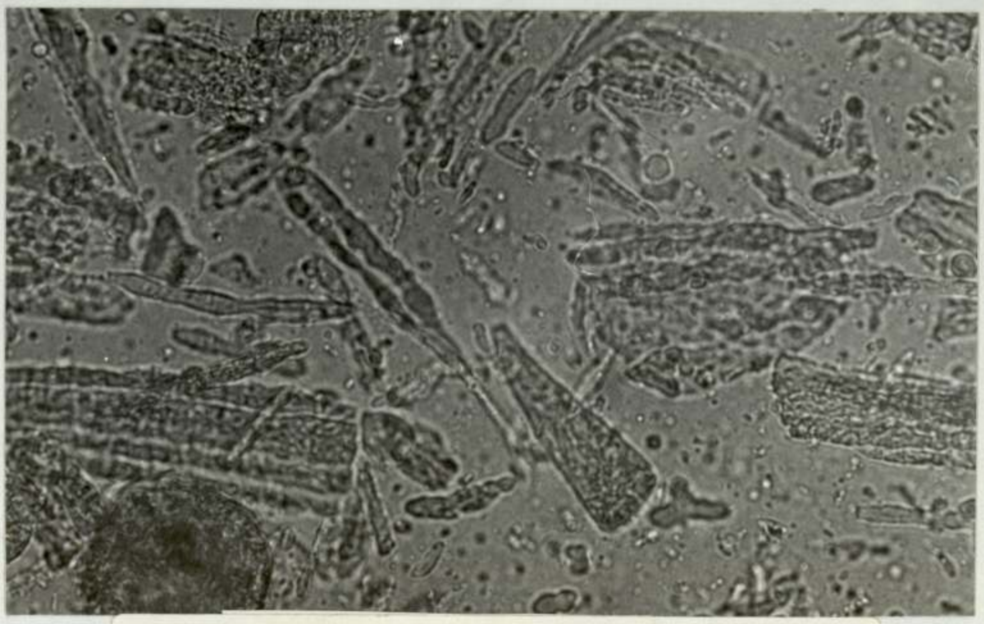


PLATE 4.14. BATCH 6
MADE WITH REDUCED ALKALI
500 x MAGNIFICATION

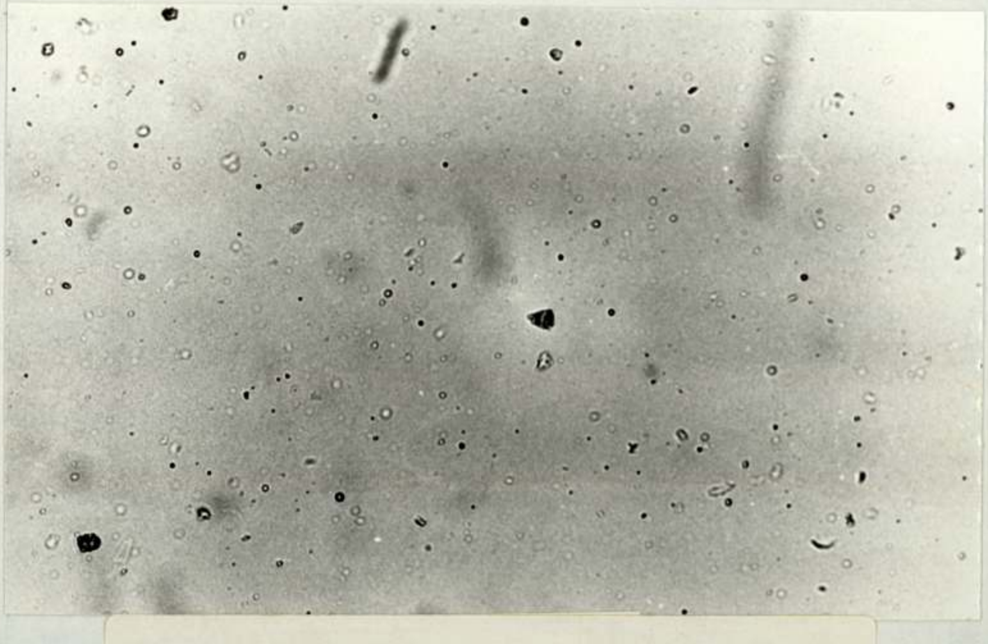


PLATE 4.15. BATCH 7
MADE WITH INCREASED ALKALI
500 x MAGNIFICATION

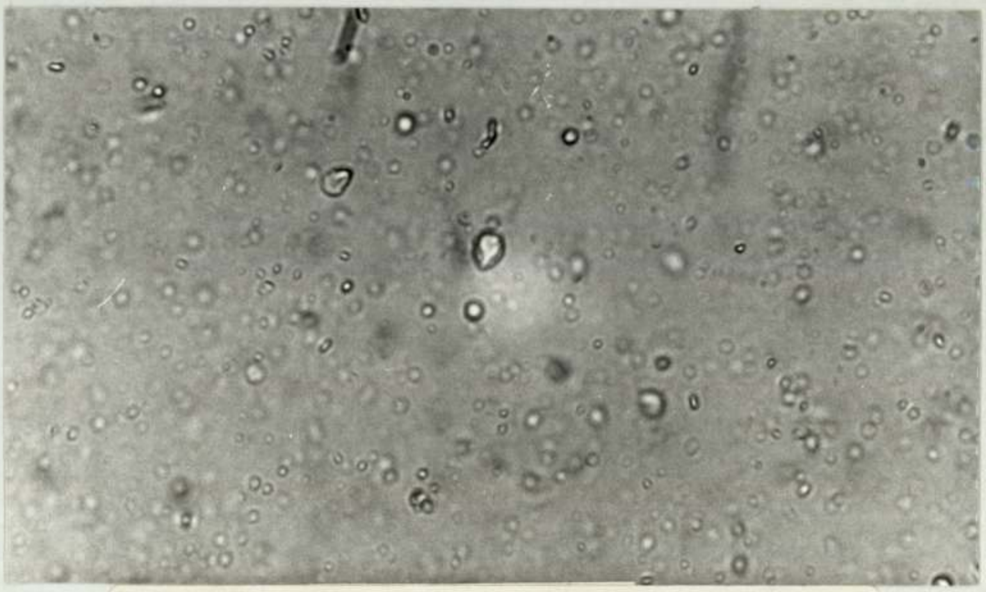


PLATE 4.16. BATCH 8
MADE WITH INCREASED ALKALI
500 x MAGNIFICATION

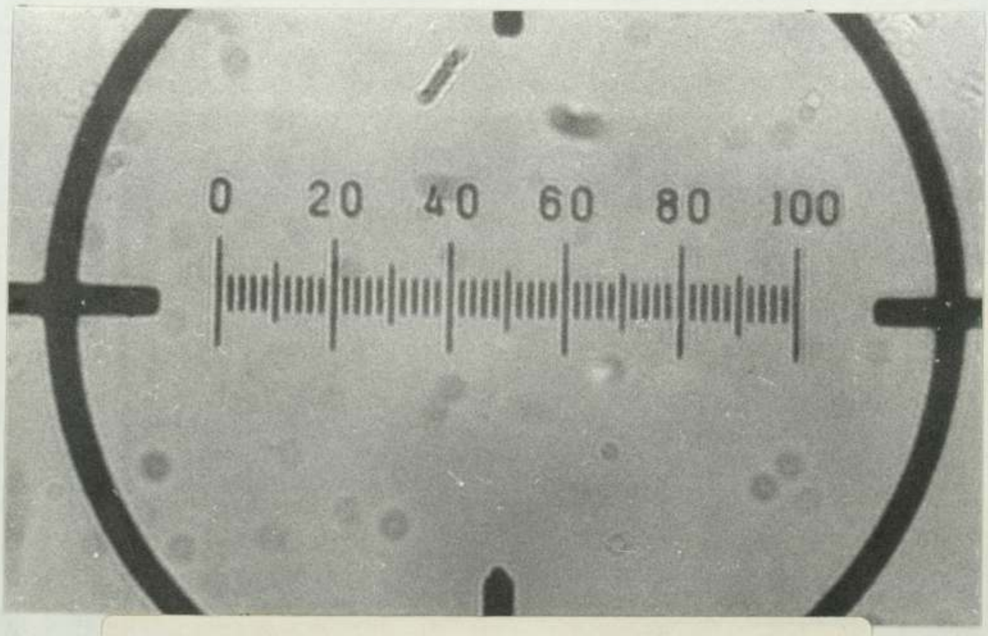


PLATE 4.17.

100 MICRON SCALE 500 x MAGNIFICATION

TABLE 4.5. - CREAMING NUMBER OF WAX EMULSIONS

BATCH REFERENCE	DETAILS OF BATCH	NUMBER OF PARTICLES GREATER THAN 10 MICRONS ON 13cm x 9cm FORMAT	EMULSION CREAMING NUMBER	OBSERVATION AFTER 24 HOURS AMBIENT STORAGE	COMMENTS ON EMULSION QUALITY
1	Standard formula and process.	4	1.3	No cream. Translucent emulsion.	Satisfactory.
2	Standard formula and process.	5	1.7	0.5mm cream. Translucent emulsion.	Satisfactory.
3	50% of formula weight of emulsifier.	8	2.7	Opaque emulsion. 15mm cream.	Unsatisfactory.
4	50% of formula weight of emulsifier.	9	3.0	Opaque emulsion. 13mm cream.	Unsatisfactory.
5	10% of formula weight of KOH used.	15	5.0	Opaque emulsion, 40mm cream and free wax.	Very bad product.
6	10% of formula weight of KOH used.	23	7.7	Opaque emulsion free wax and 50 mm cream.	Very bad product.
7	150% of formula weight of KOH.	2	0.7	Translucent. No cream.	Very clear product.
8	150% of formula weight of KOH.	1	0.3	Translucent. No cream.	Very clear product.

ambient storage after 24 hours.

Plates 4.18 to 4.20 show the effect of varying magnification on the field of view. These photomicrographs also show the range of wax particles encountered with wax emulsions. As illustrated, these particles range through the 1 micron range (which appear as dots), up to macroscopic fragments of several millimeters diameter. Each wax emulsion consists of a distribution of particle sizes and this is discussed more fully in Section 7. An alternative viewpoint is to regard a wax emulsion as consisting of a mother liquor of sub-microscopic particles, carrying various microscopic and macroscopic particles.

(d). Conclusion.

Because it is only possible to see part of the distribution, the microscopic size measurement method may only be applied to assess creaming tendency, which is caused by larger particles rising to the surface. This is discussed further in Section 4.4.4.

4.4.2. The Estimation of the Particle Size Distribution of a Wax Emulsion, by Light Transmission and the use of the information obtained to assess appearance.

(a). Introduction.

The method of Queen et.al.(46) described in Section 2

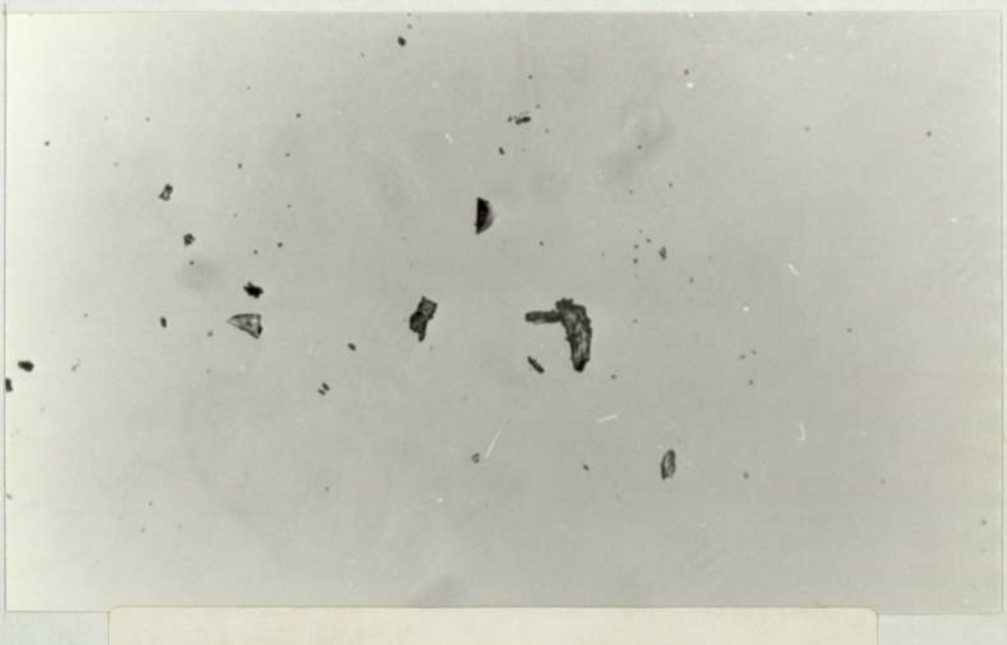
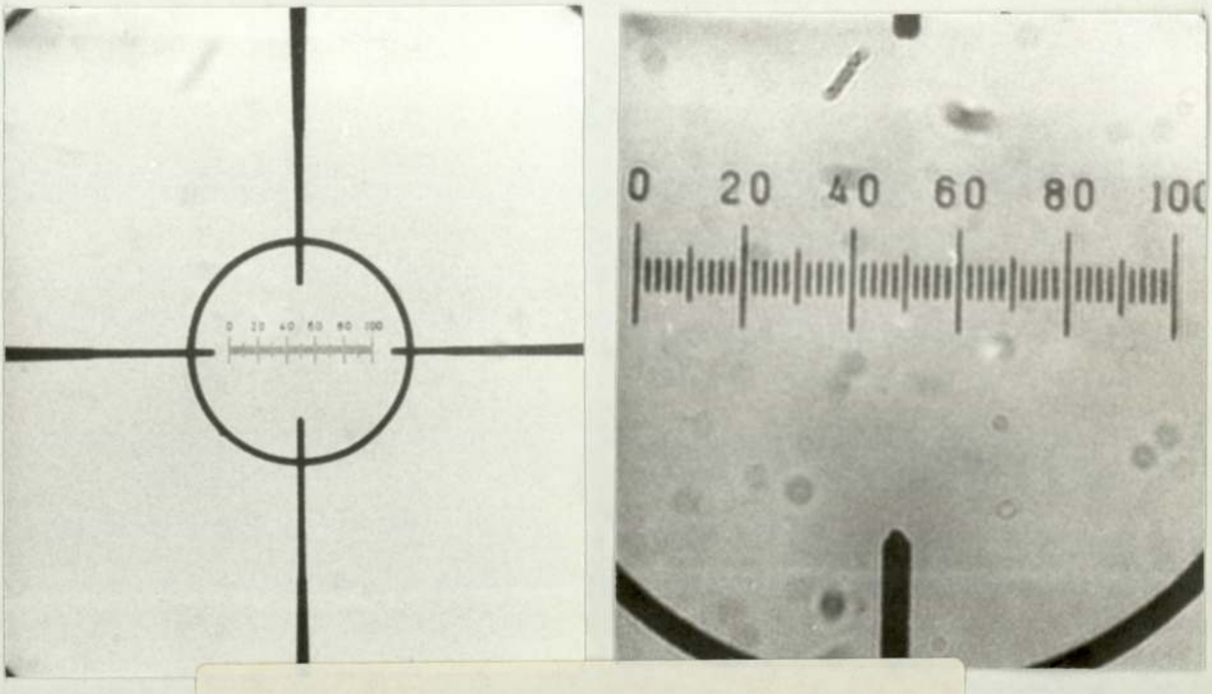


PLATE 4.18.
WAX EMULSION AT 125 x MAGNIFICATION

PLATE 4.19.
SAME WAX EMULSION AS IN PLATE 4.18.
BUT AT 500 x MAGNIFICATION SHOWING
REDUCED VIEWPOINT.



A B

PLATE 4.20.

A AT 125 x MAGNIFICATION
B AT 500 x MAGNIFICATION

was studied together with the analytical methods within Johnson Wax. The method of Queen et al was the only literature reference on particle size measurement that specifically referred to wax emulsions, though similar techniques had been developed by Johnson Wax. However, although ambitious claims with regard to the scope and value of the method were made by Queen, two limiting factors were immediately apparent as follows:-

(i) The method was not capable of yielding a wax particle size distribution and Queen had made no attempt to obtain a mean particle diameter. The fact that Queen and coworkers were content to utilise percent transmitted light is easier to understand when one reviews the theory of such extinction techniques (24) and encounters the various necessary corrections for particulate shape, colour and concentration. A basic premise that light extinction techniques only rigorously apply to monodisperse systems is a further explanation for the limited development by Queen.

(ii) These methods have been used by Johnson Wax to assess and quantify the appearance of wax and polymer emulsions but are no longer used.

However the method was seen to have several advantages namely:-

- it was rapid and easy to perform.
- it was reproducible.

- the equipment recommended by Queen was readily available.
- no major change was made to the emulsion prior to taking measurements (with exception to dilution with water).
- it was thought that a correlation of percentage light transmission and mean particle diameter might be possible between the Queen method and the somewhat more complicated and time consuming technique of particle counting on a Coulter Counter as described in Section 4.4.3. If this proved to be possible, it would eliminate the complex calculations, corrections and inaccuracies, involved in computing this parameter from percent transmitted light alone.

(b). Apparatus.

Baush and Lomb Spectronic 20 Spectrophotometer; laboratory balance and oven at 145°C; distilled water filtered through 0.2 micron membrane.

(c). Technique.

The suitability of the method to study wax emulsions was first determined by scanning typical emulsions diluted from 0.25 to 1% solids using various wave lengths. For these measurements, a Unicam scanning spectrophotometer was used and the results are shown in Figures 4.1. to 4.3. in Section (d). From the graphs, it was seen that when the study emulsion was diluted, as suggested by Queen's method (to 1% solids with distilled water), a convenient optimum wave length for a mid-scale that would give on scale instrument readings was approximately 500 nanometres

(millmicrons.) This agreed with the results of Queen et. al., and was thus adopted for further study.

Measurements were made of various batches of the study emulsion incorporating most of the range of qualities likely to be encountered in practice. These batches were then reserved for particle counting in order to obtain correlation data. At this stage it was hoped that a plot of mean particle diameter (from the Coulter Counter) - versus percentage transmission would be possible, such that future emulsions could be tested quickly and reliably.

(d). Results.

Figures 4.1., 4.2. and 4.3. show the measurements made on the study emulsion with the Unicam scanning spectrophotometer. Table 4.6. shows the percentage transmitted and light and other data obtained with various batches of wax emulsions.

(e). Discussion.

Queen's method seemed to be able to differentiate between those mother liquors (see 4.4.1.(c)), which contained substantially submicroscopic particles, and those which contained coarser particles. However, its performance on the macroscopic particles, particularly the very large ones, was less good. In fact, some emulsions which creamed badly due to large (i.e. greater than 10 micron) wax particles, transmitted light quite readily. The reasons for these

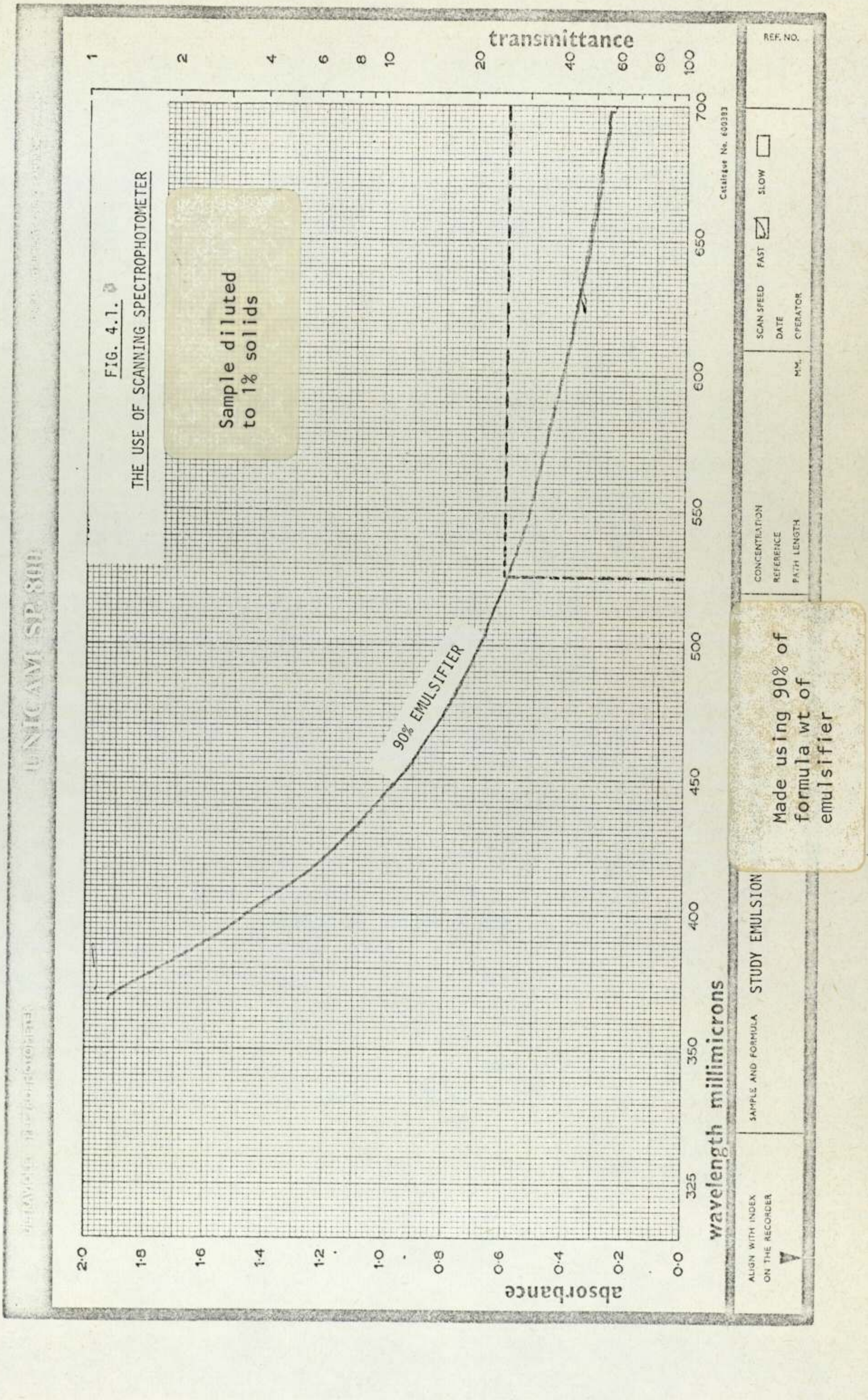


FIG. 4.1.

THE USE OF SCANNING SPECTROPHOTOMETER

Sample diluted to 1% solids

Made using 90% of formula wt of emulsifier

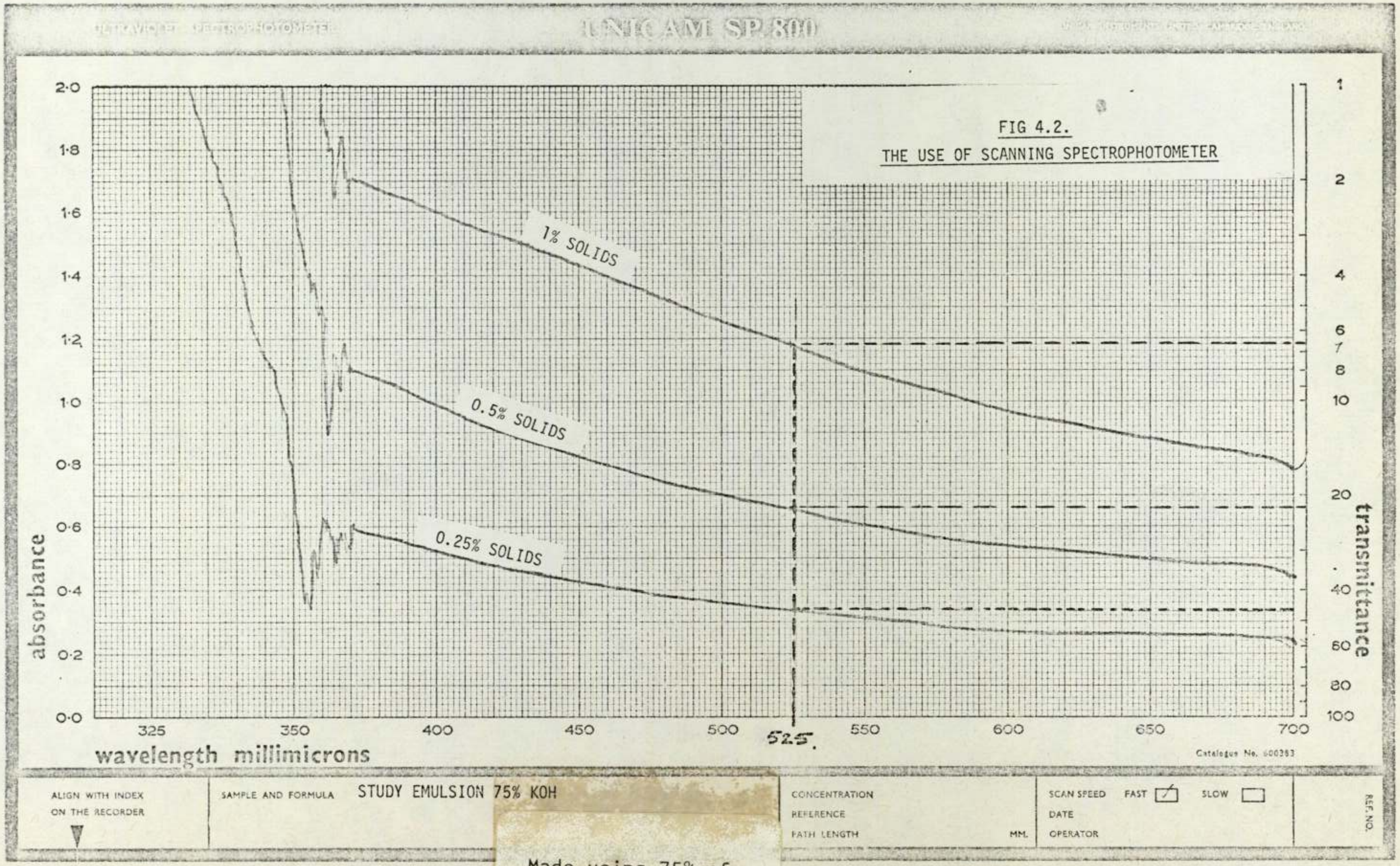


FIG 4.2.

THE USE OF SCANNING SPECTROPHOTOMETER

SAMPLE AND FORMULA STUDY EMULSION 75% KOH

Made using 75% of
formula wt of KOH
See table 4.6

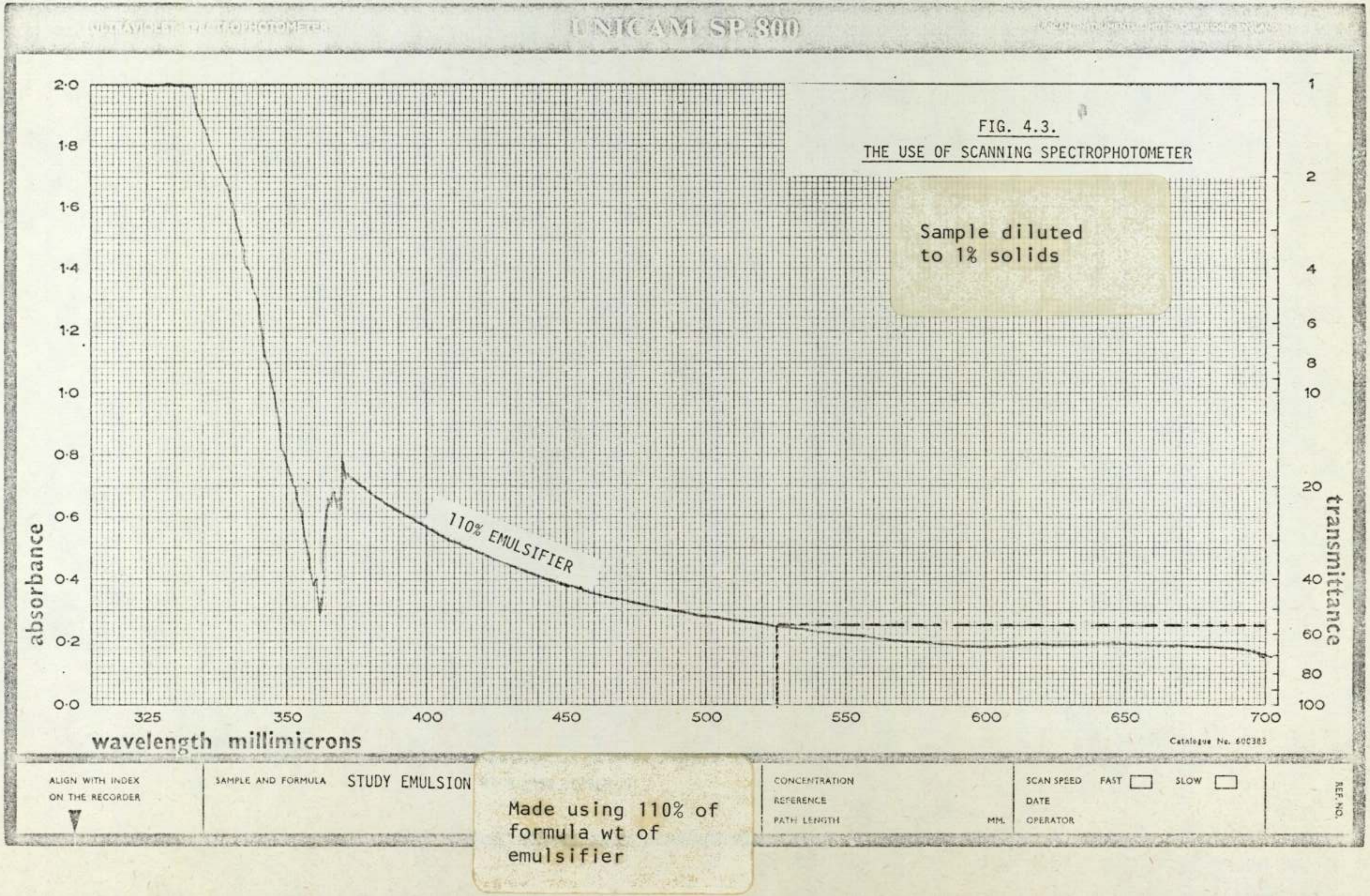


FIG. 4.3.

THE USE OF SCANNING SPECTROPHOTOMETER

Sample diluted to 1% solids

Made using 110% of formula wt of emulsifier

4.6. - LIGHT TRANSMISSION MEASUREMENTS ON THE STUDY EMULSION

BATCH REFERENCE	DETAILS	% LIGHT TRANSMISSION	24 HOUR AMBIENT STORAGE	COMMENTS ON QUALITY
1	Standard formula	36.0	No cream. Translucent emulsion.	Satisfactory.
2	Standard formula	34.5	0.5mm cream. Translucent emulsion.	Satisfactory.
3	50% of formula weight of emulsifier.	19.0	Free wax. Opaque emulsion, 15mm cream.	Unsatisfactory.
4	50% of formula weight of emulsifier.	21.0	Free wax. Opaque emulsion. 13mm cream.	Unsatisfactory.
5	10% of formula weight of KOH.	0.0	Opaque emulsion. Much free wax on surface. 40mm cream.	Very bad product.
6	10% of formula weight of KOH.	0.0	Opaque emulsion. Some free wax. 50 mm cream.	Very bad product.
7	150% of formula weight of KOH.	65.0	No cream. Very translucent emulsion.	Very clear product. Satisfactory.
8	150% of formula weight of KOH.	71.0	No cream. Very translucent product.	Very clear product.
124 ex works	Reject sample of standard formula made in works.	36.5	Translucent. Much free unemulsified wax. 30mm cream.	Unsatisfactory
Beeswax emulsion	Standard formula using Beeswax to replace AC540	0.0	Opaque. No cream.	Satisfactory though opaque.

anomalies may be the type and number of particles present in the emulsion. In most batches of the study emulsion, the greatest number of wax particles will be small i.e. submicroscopic. Therefore the numbers of microscopic and macroscopic particles will be relatively small. Consequently when the emulsion is diluted to 1% solids, few macroscopic particles are present to influence light extinction. Further, due to their bulk and shape, the effects are different from small spherical particles. Hence the percent light transmitted is largely due to the emulsion mother liquor and consequently light transmission cannot be used to reliably assess creaming.

If on the other hand, stability in terms of aggregation, coalescence, or inversion is to be evaluated, it is possible that such changes could be monitored by light transmission, providing the changes were sufficiently large.

(f). Conclusion.

Difficulties were encountered in correlating light transmission and particle size distribution. This test is only useful as an indication of quality and is most likely to be valuable in monitoring and quantifying changes.

4.4.3. Assessment of the Particle Size Distribution of a Wax Emulsion by Particle Counting and the Use of this Information to Assess Appearance.

(a) Introduction.

The third method for the particle size analysis of wax emulsions that was highlighted by the literature review was that of particle counting. Although no specific examples of the method being applied to industrial wax emulsions were found, it was considered to be attractive for the following reasons (27):-

- it was reported to have a high degree of accuracy.
- it was reported to be simple to use.
- it was reported to be a rapid method.

A programme of work was therefore undertaken to evaluate the commercially available instruments.

(b) Apparatus.

Most of the experimental work for this evaluation was carried out on a manual Coulter Counter model ZB because it was available when required and because it was claimed by the manufacturers to be a better tool for research work. However, in order to complete the evaluation of this equipment for sizing wax emulsions, some studies were undertaken on the semi automatic model TA instrument complete with data plotting equipment.

Product sampling tubes of 280, 140, 50 and 30 microns were tried using Coulter supplied and recommended electrolyte

(Isoton). Both electrolyte and the distilled water used for sample dilution and equipment cleaning were filtered on a Coulter membrane filter unit. This unit operated under vacuum and housed Gelman 0.2 micron membranes. Samples were introduced into the counter with a disposable syringe.

The counter was housed in a laboratory well isolated from electrical or acoustical disturbance and equipped for 'clean' working.

(c) Technique.

Preliminary Tests with Electrolyte:

Initially the analytical methods described in the instrument manual (126) were followed with the ZB apparatus. First the compatibility of the study emulsion with the Coulter electrolyte (Isoton), was investigated by adding samples of as made emulsions (at approximately 20% solids) and samples at various dilutions, to 25mls of filtered Isoton. The resultant mixtures were stored at ambient temperatures and at 60^{o}C and changes monitored visually and by microscope.

Particle counting tests aimed at further confirming the suitability of the electrolyte system were then carried out according to the instrument manual. During these tests it was found that although the Isoton was not totally compatible with the study emulsion, provided that the emulsion was added undiluted and readings taken within thirty minutes, the instrument would function normally. Diluted samples however, seemed to aggregate or coalesce rapidly.

Selection of Sampling Tubes:-

According to the instrument manual, it was necessary to have some information on the size range to be measured in order to select sampling tubes. From the microscopic studies conducted in Section 4.4.1., it was believed that a substantial part of the wax would be present in the submicron range. It was also known that with some (substandard) emulsions, appreciable quantities of macroscopic particles could be present which, although present in much smaller numbers, could cause problems with product appearance. It was thus important to include them in the analysis otherwise a biased result similar to that obtained with light transmission methods might be obtained. Therefore it was necessary to consider a Coulter analysis based on two tubes and consultation with Coulters indicated that the largest tube manufactured was 2000 micron or 2mm. It was further claimed that each tube should size particles between 2 and 40% of its orifice diameter. Thus the maxima and minima for particle sampling tubes were calculated and are shown in Table 4.7. below.

TABLE 4.7.

RELATION BETWEEN COULTER TUBE SIZE AND PARTICLES THAT MAY BE COUNTED

TUBE SIZE	RANGE OF PARTICLES COUNTED	COMMENTS
30	0.6 - 12 microns	Smallest tube available.
50	1.0 - 20 microns	
140	2.8 - 56 microns	
1000	20 - 400 microns	
2000	40 - 800 microns	Largest tube available.

Hence, the minimum particle that can be counted is 0.6 micron.

Hence, the maximum particle that can be counted is 800 micron.

****

From a visual examination of several industrial wax emulsions (good and bad), it was seen that even those regarded by Johnson as premier quality, contained many particles greater than 800 microns.

This was thought to be due to:-

- incomplete emulsification of the wax.
- unemulsified residues from previous batches.

In practice these particles are normally removed from the finished product by filtration.

From Table 4.7., the most convenient 2 tube analysis would have been with 50 micron and 1000 micron tubes. This was because the method required that ranges covered by the selected tubes should overlap. However, it was quite clear (by visual examination), that even with 'high quality' product, part of the top end of the distribution would be excluded from such an analysis. In addition, there were doubts also about the possibility of excluding particles at the lower end too. But at this time, 0.6 microns seemed to be a good compromise, having regard for available equipment, and the lack of comprehensive information from the microscopic studies.

Preliminary tests with 800 micron (25 mesh) sieves were conducted on a number of wax emulsions classified as satisfactory and substandard by microscopic techniques. These tests indicated that particles greater than 800 microns could be present in wax emulsions judged to be satisfactory at up to 2% by weight of the total wax present. Similarly, in substandard wax emulsions, this level could rise to 30% of the total wax present. Although a substantial part of the size distribution might not be counted by the instrument, it was decided to explore the capabilities of the technique and assess the results.

Operation.

Attention was focused on a single tube method, utilising the smallest tube (30 micron), thereby extending the scan downward to the threshold of the instrument. According to the instrument manual (126), the use of the 30 micron tube required that the sample be pre-filtered through a 10 micron mesh. This was in order to prevent tube blockage during particle counts, remembering that the maximum particle size that could be handled was 12 microns.

This technique was later modified by pre-weighing the filter cloth (127). By taking a fixed sample weight of approx. 10g (depending on the emulsion quality and concentration), and knowing the percentage by weight of wax in the emulsion, (See Section 4.3.1.), the percentage of particles greater than 10 micron were obtained. Actual weights of dry residue were measured by re-weighing to constant weight using an oven set at 145^{0}C and a desiccator. Care was taken to ensure all the wax residue was filtered by washing with a known quantity of filtered distilled water.

The less than 10 micron filtrate was then counted according to the standard single tube method devised by Coulters (126) and the appropriate dilution factor applied. A computer programme was devised to simplify the calculations, which were presented as a cumulative weight percentage greater than a stated particle diameter. These results were arranged to cover the size range from ten microns to 0.6 microns (claimed by Coulters to be the lower range of the instrument). As the Coulter method presented this cumulative weight percentage data on a 100% basis, it was then corrected for those particles greater than 10 micron according to the relation.

$$W(\%) = W' \times \frac{(100 - w)}{100} + w$$

Where W = Corrected cumulative % greater than stated size.

W' = Measured cumulative % greater than stated size from Coulter Counter.

w = % of particles greater than 10 microns.

In this way, a cumulative particle size curve was plotted. Finally, a particle diameter was obtained corresponding to the point where 50% of the particles were greater than the stated size. This diameter was regarded as the median diameter for that sample.

Unfortunately, the technique proved to be unsatisfactory in the following respects:-

(i). The particle counting via the Coulter ZB was very slow and difficult, primarily due to repeated and often prolonged blockage of the sample tube. Sample blockage could sometimes be treated quickly according to the methods in the manual (126). More often however, a large wax particle would wedge itself requiring the careful application of pressure or even solvent action to free it. Both these techniques required the apparatus to be dismantled. Hence the actual counting of sample usually took at least 30 minutes and sometimes up to 1½ hours to complete. Computation of the results required a further 20 - 30 minutes making the total time to obtain the results of the count between one and two hours.

(ii). In addition to the particle count, a further 1½ - 2 hours was required to obtain the percentage greater than 10 microns by the gravimetic method described above. Thus the total time to obtain a size distribution and median particle diameter was typically 2½ to 4 hours.

(iii). In actual practice, it was difficult to collect reliable data much below 1.3 microns due to electrical and accoustical interferences; electrolyte induced coalescence; and instrument malfunction.

(iv). There was no reliable way to determine just how much of the lower end of the distribution was being excluded except that the photomicrographic evidence suggested that a substantial fraction of the wax particles were in the submicron range.

Similar problems were encountered with the semi-automatic TA instrument except that only a few minutes were required to compute the median particle diameter, having obtained reliable data on the sample emulsion.

(d) Results:

Table 4.8. shows a typical Coulter ZB sheet with an explanation of the symbols. Figure 4.4. shows the data generated by the semi-automatic Coulter Model TA. The actual particle counts in the various size ranges may be obtained from the model TA using the interrogation switch and hand calculation methods described in the instrument manual (128). However, the instrument is normally coupled to an automatic X-Y plotter. This plot (illustrated in Figure 4.4.) presents the following data:-

(i) Accumulative percentage weight greater than stated diameter.

(ii) A weight frequency histogram (differential plot).

Table 4.9. shows residues obtained when filtering various wax emulsions through 800, 400 and 10 micron filter media showing that a substantial portion of the wax particles are macroscopic.

Table 4.10. shows Coulter data obtained with the 30 micron tube on various wax emulsions pre-filtered through 10 micron cloth.

Table 4.11. shows the computation of corrected cumulative (weight) particle size distribution for these wax emulsions incorporating the data on residues retained on 10 micron cloth from Table 4.9.

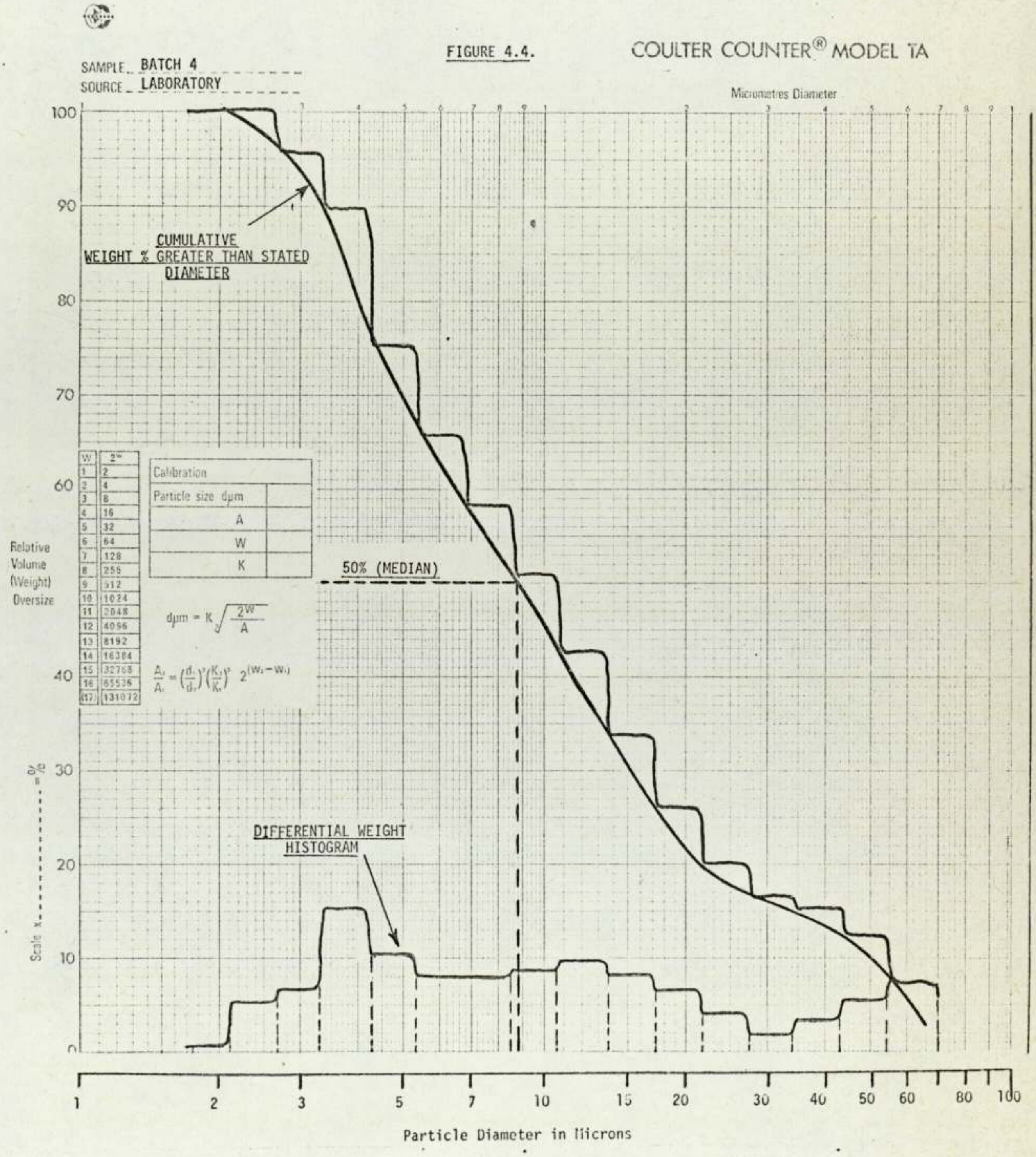


FIGURE 4.4.

COULTER COUNTER® MODEL TA
SAMPLE BATCH 4
SOURCE LABORATORY
Micrometres Diameter
CUMULATIVE WEIGHT % GREATER THAN STATED DIAMETER
50% (MEDIAN)
DIFFERENTIAL WEIGHT HISTOGRAM
Relative Volume (Weight) Oversize
Scale x ---- = %
100
90
80
70
60
40
30
20
10
0
W | 2^W
1 | 2
2 | 4
3 | 8
4 | 16
5 | 32
6 | 64
7 | 128
8 | 256
9 | 512
10 | 1024
11 | 2048
12 | 4096
13 | 8192
14 | 16384
15 | 32768
16 | 65536
(17) | 131072
Calibration
Particle size dµm
A
W
K
$d\mu m = K\sqrt[3]{\frac{2^W}{A}}$
$\frac{A_2}{A_1} = \left(\frac{d_1}{d_2}\right)^3\left(\frac{K_2}{K_1}\right)^3 2^{(W_2-W_1)}$
1
2
3
5
7
10
15
20
30
40
50
60
80
100
Particle Diameter in Microns

TABLE 4.8

INDUSTRIAL MODEL ZB & B

'COULTER COUNTER' DATA AND WEIGHT CONVERSION

SINGLE THRESHOLD

Sample.............................. Source.............................. Electrolyte.............................. Dispersant.............................. Date..............

Aperture Diameter.............................. Manometer Volume.............................. Calibration Factor, k.............................. Matching Switch.............................. Operator..............

Aperture Resistance.............................. Gain Control.............................. Coincidence Factor, p.............................. Calibration Data..............................

t_L	I	A	n' (raw counts)				$\bar{n}'$	$n'' = p\left(\frac{\bar{n}'}{1000}\right)^2$	B	$n = \bar{n}' + n'' - B$	$V = t_L.I.A$	$d_L = k\sqrt[3]{V}$	Δn	$\bar{V}$	$\Delta n.\bar{V}$	$\Sigma(\Delta n)\bar{V}$	Wt.%
1	2	3	4				5	6	7	8	9	10	11	12	13	14	15
Lower Threshold	Aperture Current	Attenuation	Counts read directly off Counter				Average of Raw Counts	Coincidence Correction	Background Count on Blank Electrolyte	True Particle Count	Relative Particle Volume	Particle Diameter (micrometres)	No. of Particles in each Successive pair of size levels (Particle Frequency)	Average relative particle Volume	Total Volume of all particles in given size ranges	Total Volume of all particles in whole size range	Cumulative Volume (Weight) Percentage above stated size

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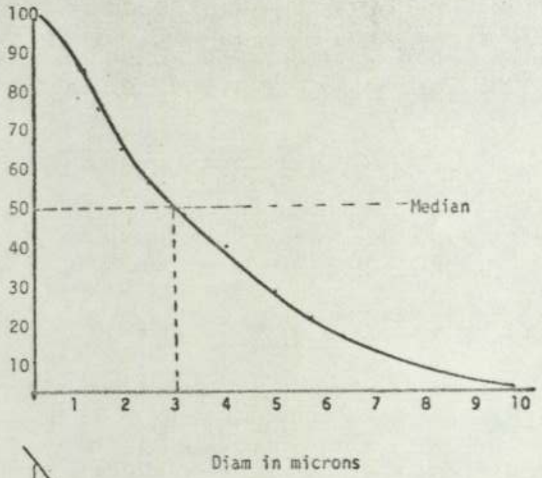
TABLE 4.9. - WAX EMULSION RESIDUES ON VARIOUS FILTER MEDIA

BATCH REFERENCE	PERCENT GREATER THAN 850 MICRONS	PERCENT GREATER THAN 450 MICRONS	PERCENT GREATER THAN 10 MICRONS	COMMENTS
1	0.107	0.194	0.205	Standard laboratory batch.
3	5.309	15.217	23.404	Laboratory batch using 50% of emulsifier. Considerable creaming.
5	8.722	11.041	13.793	Laboratory batch using 10% of formula weight of KOH.
8	Not retained	Not retained	0.157	Very clear emulsion with little suspended wax.
Normal works batch 163	0.135	0.168	0.195	Standard works quality.
11	29.101	32.761	38.235	Made using 50% of emulsifier and reduced strength KOH. Very bad separation.

TABLE 4.10. - DATA ON 30 MICRON TUBE

BATCH REFERENCE	PARTICLE DIAMETER MICRONS	PERCENT WAX GREATER THAN STATED DIAMETER
1	9.99	1.81
	7.94	8.09
	6.30	16.17
	5.00	29.02
	3.97	39.86
	3.15	48.65
	2.50	56.91
	1.98	66.01
	1.58	74.93
	1.25	86.42
	0.99	100.00
3	9.99	5.40
	7.95	15.73
	6.30	26.49
	5.00	39.12
	3.97	50.64
	3.15	60.97
	2.15	67.78
	1.98	74.95
	1.58	82.33
	1.22	91.52
	0.99	100.00



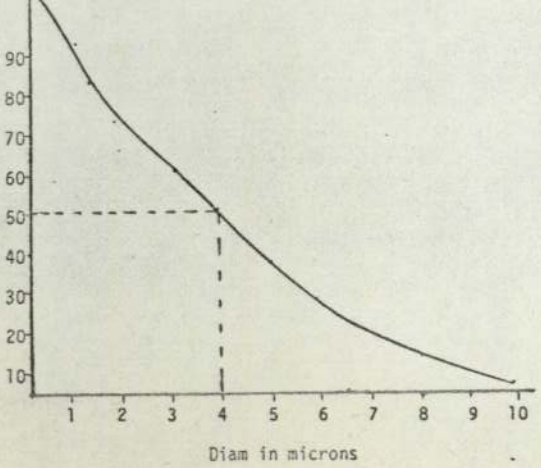
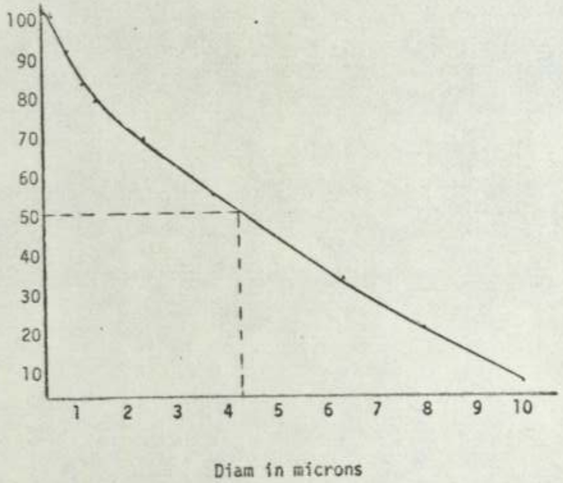


TABLE 4.10. - DATA ON 30 MICRON TUBE CONTINUED

BATCH REFERENCE	PARTICLE DIAMETER MICRONS	PERCENT WAX GREATER THAN STATED DIAMETER
5	9.99	7.16
	7.94	21.39
	6.30	33.94
	5.00	44.33
	3.79	54.35
	3.15	63.18
	2.50	68.96
	1.98	72.79
	1.58	78.10
	1.25	83.10
	0.99	92.07
	0.79	100.00
11	9.99	7.16
	7.94	22.50
	6.30	32.57
	5.00	45.47
	3.97	51.71
	3.15	62.91
	2.50	71.72
	1.98	80.98
	1.58	85.42
	1.25	92.50
	0.99	100.00



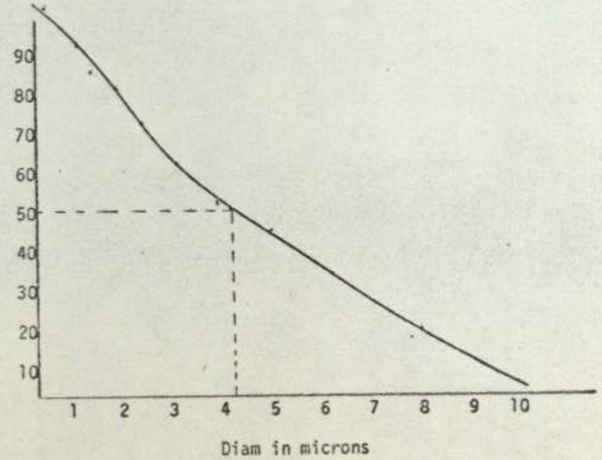


TABLE 4.10. - DATA ON 30 MICRON TUBE CONTINUED

BATCH REFERENCE	PARTICLE DIAMETER MICRONS	PERCENT WAX GREATER THAN STATED DIAMETER
163	9.99	2.26
	7.94	6.61
	6.30	12.04
	5.00	17.99
	3.97	26.29
	3.15	36.70
	2.50	48.72
	1.98	60.58
	1.58	72.37
	1.25	83.97
	0.99	100.00

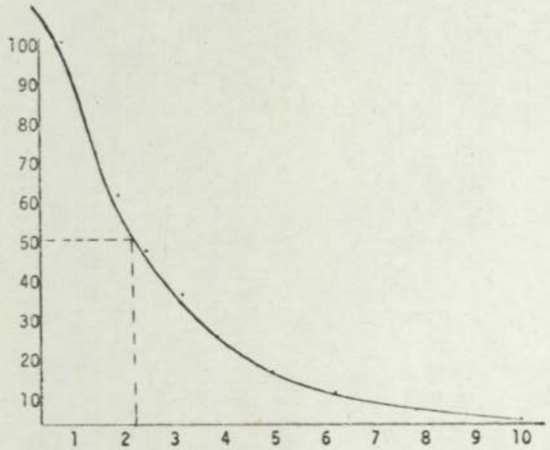


TABLE 4.11. - CORRECTED PARTICLE SIZE DISTRIBUTION INCORPORATING PERCENT GREATER THAN 10 MICRONS

BATCH REFERENCE	PARTICLE DIAMETER	PERCENT GREATER THAN STATED SIZE W'	PERCENT GREATER THAN 10 MICRONS w	$\frac{(100 - w)}{100}$	$\frac{(100 - w)W'}{100} + w$
1	9.99	1.81	0.201	0.998	2.01
	7.95	8.09	0.201	0.998	8.28
	6.30	16.17	0.201	0.998	16.34
	5.00	29.02	0.201	0.998	29.16
	3.97	39.86	0.201	0.998	39.98
	3.15	48.65	0.201	0.998	48.75
	2.50	56.91	0.201	0.998	57.00
	1.98	66.01	0.201	0.998	66.08
	1.58	74.93	0.201	0.998	74.98
	1.25	86.42	0.201	0.998	86.45
	0.99	100.00	0.201	0.998	100.00
3	9.99	5.40	23.404	0.766	27.54
	7.95	15.73	23.404	0.766	35.45
	6.30	26.49	23.404	0.766	43.69
	5.00	39.12	23.404	0.766	53.37
	3.97	50.64	23.404	0.766	62.20
	3.15	60.97	23.404	0.766	70.10
	2.50	67.78	23.404	0.766	75.32
	1.98	74.95	23.404	0.766	80.81
	1.54	82.33	23.404	0.766	86.46
	1.25	91.52	23.404	0.766	93.51
	0.99	100.00	23.404	0.766	100.00

TABLE 4.11. - CORRECTED PARTICLE SIZE DISTRIBUTION INCORPORATING PERCENT GREATER THAN 10 MICRONS CONTINUED

BATCH REFERENCE	PARTICLE DIAMETER	PERCENT GREATER THAN STATED SIZE W'	PERCENT GREATER THAN 10 MICRONS w	$\frac{(100 - w)}{100}$	$\frac{(100 - w)W'}{100} + w$
5	9.99	7.16	13.793	0.862	19.97
	7.94	21.39	13.793	0.862	32.23
	6.30	33.94	13.793	0.862	43.05
	5.00	44.33	13.793	0.862	52.01
	3.97	54.35	13.793	0.862	60.65
	3.15	63.18	13.793	0.862	68.26
	2.50	68.96	13.793	0.862	73.24
	1.98	72.79	13.793	0.862	76.54
	1.58	78.10	13.793	0.862	81.12
	1.25	83.10	13.793	0.862	85.43
	0.99	92.07	13.793	0.862	93.16
	0.79	100.00	13.793	0.862	100.00
11	9.98	7.16	38.235	0.618	42.66
	7.94	22.50	38.235	0.618	52.13
	6.13	32.57	38.235	0.618	58.35
	5.00	45.47	38.235	0.618	66.32
	3.97	51.71	38.235	0.618	70.17
	3.15	62.91	38.235	0.618	77.09
	2.50	71.72	38.235	0.618	82.53
	1.98	80.98	38.235	0.618	88.25
	1.58	85.42	38.235	0.618	90.99
	1.25	92.50	38.235	0.618	95.37
	0.99	100.00	38.235	0.618	100.00
163	9.98	2.26	0.195	0.998	2.45
	7.94	6.61	0.195	0.998	6.79
	6.30	12.04	0.195	0.998	12.22
	5.00	17.99	0.195	0.998	18.15
	3.97	26.29	0.195	0.998	26.44
	3.15	36.70	0.195	0.998	36.83
	2.50	48.72	0.195	0.998	48.82
	1.98	60.58	0.195	0.998	60.65
	1.58	72.37	0.195	0.998	72.43
	1.25	83.97	0.195	0.998	84.00
	0.99	100.00	0.195	0.998	100.00

(e) Conclusions.

The particle counting method is not a satisfactory way of obtaining a particle size distribution due to equipment problems, time requirement, need for a skilled operator and limitations on size range detectable - not below about 1.3 micron or above 800 micron.

The technique of accurately filtering out part of the size range was found to be a simple and reliable method of determining the weight fraction of wax existing above a certain size. This technique is developed in the following section.

4.4.4. Gravimetric Method for Assessing Wax Emulsion Appearance.

(a). Introduction.

Apart from the actual separation of wax and water, the next most serious effect on emulsion appearance is for it to form a creamy layer on the surface. With many substandard emulsions, the wax particles in the cream layer gradually pack tighter and tighter at the same time squeezing out water. Eventually, a situation is reached where the cream layer becomes almost solid, adhering to the container walls and preventing the removal of emulsion product. Therefore, as part of the quality assessment process, it is important to determine if the wax emulsion being examined is capable of creaming and if so, to what extent.

(b). Theoretical Considerations.

Wax particles above a certain size tend to migrate to the liquid surface because they are less dense than the surrounding (mostly aqueous) medium. Stokes (129) studied the effects of sedimentation for particles of different sizes and densities and produced a relationship between the downward velocity of a particle, its radius and the density difference between the particle and the surrounding medium. In the case of wax emulsions, sedimentation rarely occurs, the wax particles moving upwards. However apart from the direction of movement (or alternatively the sign of the velocity term in the equation), Stokes Law may be used to calculate the rate at which a wax particle of a certain radius will move upward to the liquid surface. Hence it is possible to determine for a given height of liquid, how long creaming will take to occur.

Conversely if a standard liquid height is specified, the time required to produce cream may be correlated with particle size. When this is done, it is possible to see the particulate size range which causes creaming, because those particles which take several months to a year to cream may be disregarded for practical purposes. If the minimum particle size is computed which causes creaming in a given time of approximately 24 hours, and if it is possible to accurately filter the emulsion sample through a medium capable of retaining this particle size, then the creaming tendency may be estimated by weighing the residue and expressing it as a percentage of the total wax present in the emulsion. The greater the percentage of wax greater than this minimum particle size, the greater will be the tendency of the wax emulsion to cream.

The original Stokes Law relationship is:-

$$u = \frac{2gr^2(d_1 - d_2)}{9n_2}$$

where u = rate of migration to the surface cm/sec.

g = acceleration due to gravity - cm sec^{-2}.

r = particle radius - cm.

d_1 = density of particle $\mathrm{g/cm}^3$ (usually the oil/wax phase.

d_2 = density of continuous phase (usually the aqueous phase.

n_2 = viscosity of continuous phase in poise.

Various modifications to this relationship have been made to take account of the hindering effect of other particles and the viscosity of the disperse phase by Rybczynski (130) and Hadamard (131) and others (132). However, it seems that experimental studies correlate best with the above relationship and accordingly this has been used (133).

Further constraints are evident from a consideration of available filter media and the physical difficulty of filtering even small volumes of wax emulsions through small porosity septa.

(c). Apparatus.

The following apparatus was used:-

Coulter (Beckman type) vacuum funnel and sintered glass filter holder; Simon filter cloth; metal foil drying crucibles; laboratory balance; oven at 145^{o}C; desiccator.

(d). Technique.

Using samples of the study emulsion, various filter media were tried with pore sizes from 0.2 microns to 25 microns, to determine the problems of collecting particles above each filter pore size. The smallest sized filter media that gave a satisfactory performance in terms of short term requirement, efficiency and ease of handling was 10 micron.

The possibility of removing all water from the collected residue was explored using a laboratory oven and desiccator. Temperatures up to 145^{o}C were utilised in an attempt to minimise drying time. Finally, a satisfactory test method was established as follows:-

Approximately 10 grams of the wax emulsion were accurately weighed into the Coulter membrane filter equipped with a 10 micron membrane. By applying vacuum, the product was filtered, leaving a semi-dried residue on the filter cloth. The unit was then carefully dismantled and the cloth transferred with tweezers to an aluminium foil crucible. This crucible (already previously weighed with the filter cloth), was then transferred to a drying oven preset at 145^{0}C. After one hour it was transferred to a desiccator to cool and then re-weighed.

The percentage weight of wax particles greater than 10 microns were given by the relation:-

% wax greater than 10 micron =

$$\frac{\text{Weight of dried retained wax}}{\text{Non volatile content of emulsion x sample weight}} \quad \text{x} \quad 100\%$$

The non volatile content of the test emulsion may be determined by using the same oven and at the same time as the filtered wax is being dried.

(e). Results.

Table 4.12. shows the relationship between diameter of the wax particle (SG = 0.916) and time required to rise a distance of 10 cms (the normal depth of emulsion in a 250ml glass sample bottle). Figure 4.5. shows the results graphically.

Table 4.13. shows the results of filtration tests on several samples of the study emulsion with various filtration media and Table 4.14. shows the results of the proposed method with various wax emulsions. Comparisons with other methods are made in Section 4.5.

(f). Conclusions.

TABLE 4.12. - CREAMING RATES OF WAX PARTICLES

PARTICLE DIAMETER IN MICRONS	RISING VELOCITY cm/hr	TIME TO RISE 10cms	COMMENTS
0.5	$\frac{1.648}{10^3}$	6070 hours	7 months These particles do not cause appearance problems.
1	$\frac{6.59}{10^3}$	1517 hours	9 weeks
2	0.026	379 hours	2¼ weeks
4	0.106	95 hours	4 days
8	0.422	24 hours	Judged by visual tests these particles seem to be the start of appearance problems.
10	0.659	15 hours	
20	2.637	4 hours	Rapid cream formation. These particles definitely cause appearance problems.
50	16.481	30 mins.	Rapid cream formation.
100	65.923	9 mins.	Rapid cream formation.

FIGURE 4.5. - CREAMING VELOCITIES OF WAX PARTICLES

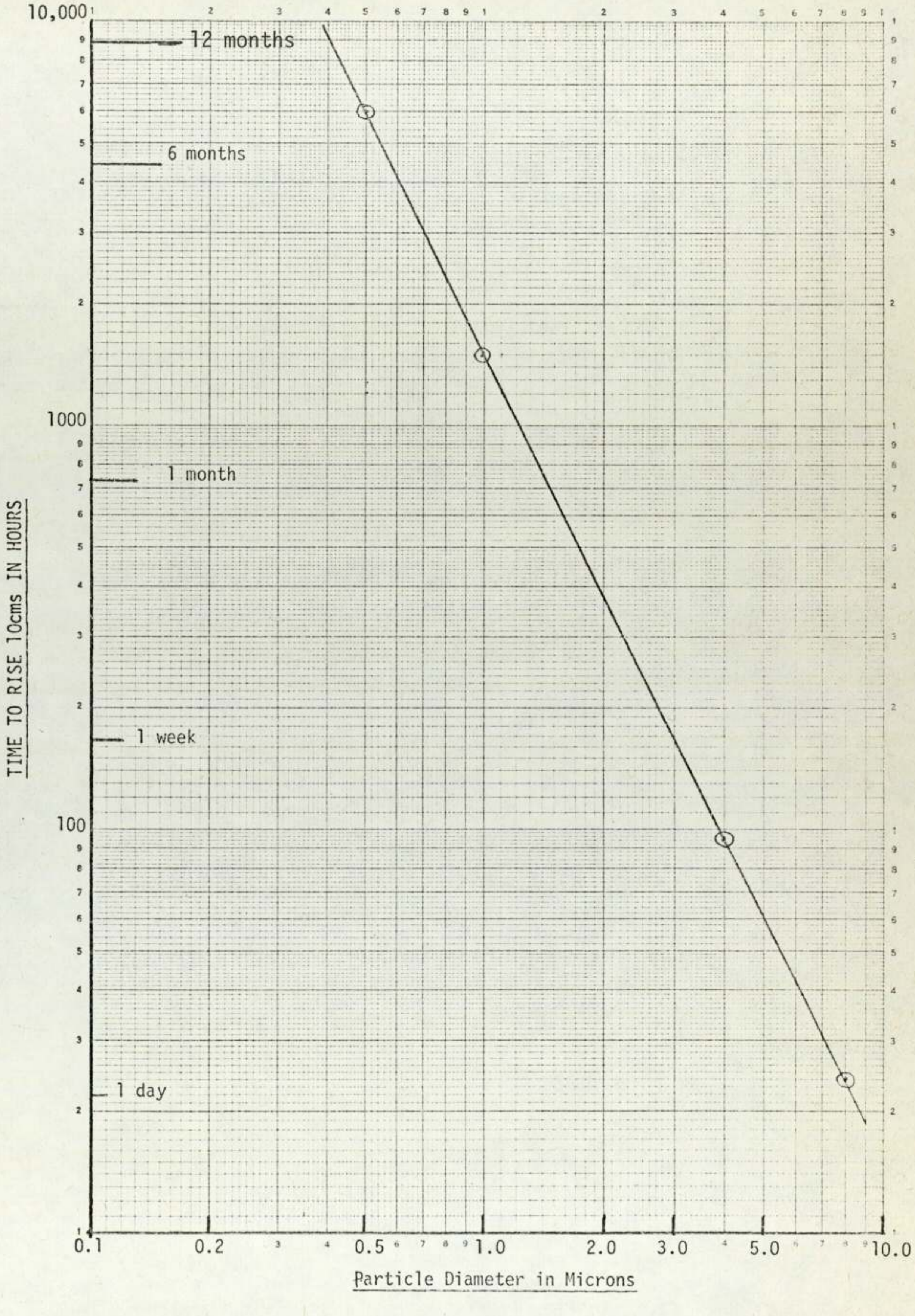


TABLE 4.13. - FILTRATION TESTS WITH WAX EMULSIONS

EMULSION QUALITY	SAMPLE REFERENCE	WEIGHT OF SAMPLE	FILTRATION MEDIUM	TIME TO FILTER ON COULTER VACUUM UNIT (126)	COMMENTS
Good	Batch 1	10g	20 micron cloth	2 mins.	Satisfactory.
Poor	Batch 3	10g	20 micron cloth	2½ mins.	Satisfactory.
Bad	Batch 5	10g	20 micron cloth	2 mins.	Satisfactory.
Good	Batch 163	10g	20 micron cloth	2 mins.	Satisfactory.
Very bad	Batch 11	10g	20 micron cloth	5 mins.	Satisfactory.
Good	Batch 1	10g	10 micron cloth	3 mins.	Satisfactory.
Poor	Batch 3	10g	10 micron cloth	5 mins.	Satisfactory.
Bad	Batch 5	5g	10 micron cloth	2 mins.	Satisfactory.
Good	Batch 163 Ex works	10g	10 micron cloth	3½ mins.	Satisfactory.
Very bad	Batch 11	5g	10 micron cloth	10 mins.	Sample filtered with some difficulty.
Good	Batch 1	10g	5 micron cloth	10 mins.	Sample not filtering properly. Much washing with distilled water required.
Good	Batch 1	5g	5 micron cloth	10 mins.	Sample still not dewatering properly.
Good	Batch 1	5g	0.2 micron membrane	Not achieved.	Even with full vacuum, filtration was not possible due to medium becoming immediately blinded.

TABLE 4.14.

GRAVIMETRIC METHOD FOR PERCENT WAX GREATER THAN 10 MICRON

EMULSION QUALITY	BATCH* REFERENCE	NON VOLATILE CONTENT	SAMPLE SIZE g	DRIED RESIDUE ON CLOTH g	PERCENT WAX GREATER THAN 10 MICRONS
Good	1	19.4720	10.0170	0.0040	0.205
Good	2	18.1013	10.2163	0.0036	0.195
Poor	3	17.4204	10.0073	0.4080	23.404
Poor	4	15.8942	10.1409	0.2981	18.495
Bad	5	16.6511	5.0337	0.1156	13.793
Bad	6	17.4225	5.3191	0.0844	9.103
Good	7	21.2444	10.0685	0.0032	0.150
Good	8	20.6327	10.0068	0.0033	0.157
Good	9	18.2313	10.0177	0.0042	**0.230 (0.238),(0.205),(0.241)
Good	10	17.4943	10.0096	0.0037	***0.211 (0.226),(0.207),(0.218)
Very bad	11	12.0543	5.0016	0.2305	****38.235 (24.916), (35.190),(28.763)

*For details see Tables 4.1. and 4.9.

Repeat tests in parenthesis.

**Mean = 0.229; Standard Deviation = 0.014
***Mean = 0.216; Standard Deviation = 0.007
****Mean = 31.776; Standard Deviation = 5.232

(f). Conclusions.

This method gives reliable information for the proportion of wax existing as particles above 10 micron. This correlates well with creaming effect and provides a convenient, quick and reliable method for quality control from an appearance viewpoint.

4.5. Comparison of Existing and Newly Developed Techniques for the Assessment of Wax Emulsion Appearance (Particle Size).

4.5.1. Methods Available.

The existing methods for assessing wax emulsion appearance have been discussed in Section 4.1. and may be summarised as:-

(a) Visual examination of light transmission.
(b) Measurement of light transmission by spectrophotometer.
(c) Centrifugation - recording extent of separation.
(d) Ambient storage and observation of extent of creaming.
(e) Hand pouring down polished glass plate.

Of these, (a), (c), (d) and (e) are currently used in Johnson Wax.

The methods that were not discovered in the literature survey and which were investigated and developed during the study are:-

(f) Photomicrographs for the identification of the type of wax particulates present and the measurement of Emulsion Creaming Number. (Section 4.4.1b.).

(g) Particle counting via Coulter Counter.

(h) The gravimetric determination of the percentage by weight of wax existing as greater than 10 micron particles.

4.5.2. Comparison.

As explained in Section 4.1., it is not entirely clear what the existing methods (a) to (e) actually measure, and they can only be justified by a history of providing adequate controls. With an increasing range of products and an increasingly critical consumer, the need for a more absolute measure of quality is growing, and this has led to the development of the new techniques (f) to (h).

The range of traditional and new methods are summarised in Table 4.15. which also includes comments on the time requirement; sensitivity, accuracy and reliability. The tests are roughly ranked in terms of effectiveness from 10 the most effective test, down to 2, the least effective test. This includes consideration of usefulness of result, time requirement, and skill requirement.

A full particle size analysis is probably unnecessary as it is only the larger particles above about 10 - 20 micron which are likely to adversely affect emulsion appearance by creaming, separation and lumpiness. When fine particles are important in assessing appearance, light transmission can be

TABLE 4.15. - COMPARISON OF METHODS FOR ASSESSING WAX EMULSION APPEARANCE

CLASSIFICATION	DESCRIPTION	TYPE OF RESULT	TESTING TIME	APPROXIMATE COST OF APPARATUS	COMMENTS
Light Transmission.	Visual inspection.	Qualitative.	5 minutes.	None required.	Usually applied without a comparative standard and therefore somewhat subjective Very easy to perform and widely used. It does not give good assessment of creaming.
Light Transmission.	Spectrophotometer.	Quantitative and qualitative percentage transmitted light or optical density.	1¼ hours.	£1200.	The test is similar to the one above except that it is quantitative. It does not give good assessment of creaming.
Creaming tendency.	Centrifuge test.	Depth or percentage of cream.	25-30 minutes.	£300.	The method is not very sensitive and can only detect major differences in quality.
Creaming tendency.	Ambient storage.	Depth of cream formed to a given time interval.	From hours up to a year.	None required.	This is the standard appearance test to which all accelerated testing methods must correlate. It is a direct assessment of product appearance with time.
Creaming tendency.	Black glass plate.	Qualitative and subjective assessment of microscopic wax particles in the emulsion.	5 minutes.	None required.	Only very approximate side by side comparisons are possible The test is widely used by polish manufacturers.
Creaming tendency.	Photomicrographs.	Quantitative via emulsion creaming number.	2 hours to several days.	£2500-3000.	Rapid visual assessments are possible but a quantitative test is somewhat slow. Only recommended for extrudable wax
Creaming tendency.	Gravimetric test.	Quantitative percentage of wax existing as particles above 10 micron.	1½ hours.	£250.	This is most reliable method for assessing wax emulsion appearance. It is easy to perform and gives reproducible results.
Size distribution and mean particle diameter.	Particle size analysis (Particle Counting).	Quantitative.	2½-4 hours.	£2500-4000.	Not recommended. Instrument cannot size all of the particles.
Size distribution and mean particle diameter.	Particle Size Analysis (Photomicrographs).	Quantitative.	2 hours to several days.	£2500-3000.	Not recommended. Instrument cannot size all of the particles.

an acceptable alternative.

4.5.3. Conclusions.

It is believed that the newly developed techniques will make quality control for appearance both more reliable and more rapid. These new tests, particularly the gravimetric test, have now been introduced as standard test procedures within the Company.

4.6. Techniques for the Assessment of Wax Emulsion Performance - Investigated and Developed during this Study.

As most wax emulsions are used in constituents of some finished product, it is likely that the only way to evaluate performance is via stability testing. The literature review in Section 2 concluded that test methods based on Centrifugation and Freeze/Thaw cycling were most promising. Accordingly these were investigated and are described below.

4.6.1. Determination of Wax Emulsion Stability by Centrifugation.

(a). Introduction.

From Section 2, it was seen that the ultra centrifuge had been used to assess emulsion stability. Unfortunately, this equipment was not available for the study and so a standard laboratory centrifuge was tried.

(b). Apparatus.

The studies were conducted using a Janetzki laboratory centrifuge with a 10cm radius and speed capability of 4000 rpm (equivalent to 1790g). Samples were contained in the same 25ml screw topped bottles used for accelerated storage (and later, freeze/thaw studies), in order that comparisons could be made.

(c). Technique.

From Section 2, and Becher's proposal (1) that centrifugation at 3750 rpm in a 10cm radius centrifuge for five hours would be equivalent to the effect of gravity for 1 year; a method was developed whereby 25 ml samples were spun at the above speed for 25 minutes to simulate the effect of gravity for one month. The results were compared with the ambient and accelerated storage tests described in Section 4.3.2. (Batches 1 to 10).

(d). Results.

The results of the tests described above are presented in Plate 4.21. and in Table 4.16. and compared later in Section 4.7 where conclusions are also drawn.

4.6.2. Determination of Wax Emulsion Stability by Freeze/Thaw Cycling.

(a). Introduction.

1 6 3 8

PLATE 4.21.

Centrifugal Stability Tests at 3750 r.p.m.
(Batch Numbers Shown Below Samples)

See Table 4.16

TABLE 4.16. - CENTRIFUGAL STABILITY STUDIES

SAMPLE REFERENCE	BATCH 1	BATCH 1	BATCH 1	BATCH 1	BATCH 2	BATCH 3	BATCH 4	BATCH 5	BATCH 6	BATCH 7	BATCH 8	BATCH 9	BATCH 10
CENTRIGURE SPEED r.p.m.	4500 (max)	4500	4500	3750	3750	3750	3750	3750	3750	3750	3750	3750	3750
DURATION OF SPIN (MINS)	300	30	25	25	25	25	25	25	25	25	25	25	25
MEASURED DEPTH OF CREAM (mm)	1	1	1	1	1	2	3	14	16	No cream	No cream	1	1

Because the existing methods and the centrifugation test appeared to yield mainly information on creaming rather than stability, it was decided to develop alternative test methods. The objective of this development was to devise a quick and reliable method for testing wax emulsion stability. Information presented in Section 2 suggested that freeze/thaw cycling might provide a suitable method.

(b). Theory of Freeze/Thaw Cycling for Stability Assessment.

A satisfactory wax emulsion is stable because of the protective emulsifier layer which surrounds each wax particle and prevents coalescence or aggregation with other wax particles. An alternative explanation is that the wax particles are held apart by electrical double layers induced by the presence of emulsifier molecules. If however, these protective forces are overcome by other forces within the emulsion, then major changes in appearance are likely to occur. During freezing, water crystals are formed which might incorporate the emulsifier also. The phase change resulting from a freeze cycle, produces forces which overcome or disrupt the stabilising forces responsible for holding the emulsion together. Major changes occur which may be observed visually when the emulsion is thawed out and liquid once more. The thawing process can also subject the test emulsion to further stress and the results are generally viewed when ambient temperature is re-attained. Such a process constitutes one freeze/thaw cycle. If the protective emulsifier layer is well established such as in a satisfactory emulsion, its ability to withstand the forces induced by freeze/thaw cycling will be increased. Hence well formed emulsions will withstand many cycles whereas those with reduced stability will not.

Changes were found to take the form of extreme viscosity increase up to the loss of mobility and sometimes complete separation of wax and water. These changes tended invariably to be well defined and not gradual. The number of cycles required to effect such changes were therefore used to assess wax emulsion stability.

(c). Apparatus.

Two alternative methods were devised comprising either:-

(i). Deep freeze unit of laboratory fridge/freezer; 25 ml sample bottles equipped with rubber bung and -35 to +50^{0}C thermometers; minute timer with alarm bell; laboratory oven set at 60^{0}C.

(ii). 10oz aerosol can; cylinder of Freon 12; 20 ml diameter pyrex sample tubes; -35 to +50^{0}C thermometer.

(d). Preliminary Experimental Work.

Initially the laboratory fridge/freezer was chosen to effect the freeze cycle. Experiments were conducted to investigate the effect of the following variables on the change in emulsion appearance:-

(i) Variation of freeze temperature from -1°C to 25°C (limit of deep freeze apparatus).
(ii) Variation of the rate of freezing.
(iii) Variation in the rate of thawing.

The results of these experiments are presented in Table 4.17. from which it was concluded that the temperature differences and rates of freezing or thawing are relatively unimportant as long as the sample is completely frozen or completely thawed.

The time required to assess the stability of many emulsions still ran to several hours (1 freeze/thaw cycle took 35 minutes and usually at least two more were required), and attempts were made therefore to develop a more rapid method. During the initial experimental work, the effect of rate of freeze was studied by freezing the emulsion rapidly with Freon 12. An apparatus was assembled to use this method to shorten freeze time, the thaw method remaining unchanged.

(e). Test Methods.

(i). Using Freezer.

A 25 ml glass bottle equipped with a thermometer and closed with a rubber bung to permit expansion was filled with sample and placed in the freezer cabinet controlled at -25°C. A minute timer was set to 30 minutes.

TABLE 4.17. - VARIATION OF FREEZE/THAW PARAMETERS

BATCH REFERENCE	FRIDGE TEMPERATURE °C	TIME TO REACH -1°C	TYPE THAWING	TIME TO REACH +5°C	NUMBER OF FREEZE THAW CYCLES TO MAJOR CHANGE IN APPEARANCE
Batch 3	-25	Approximately 4 hours to reach -20°C.	Ambient	Approximately 5 hours.	3
Batch 3	-25	Approximately 4 hours to reach -19°C.	Oven at 60°C.	5 minutes.	4
Batch 1	-25	Approximately 4 hours to reach -21°C.	Oven at 60°C.	5 minutes.	Greater than 10
Batch 1	-5	Approximately 2 hours.	Ambient.	Approximately 2 hours.	Greater than 10
Batch 1	-15	1½ hours.	Ambient.	Approximately 2½ hours.	Greater than 10
Batch 1	-25	25 minutes.	Ambient.	Approximately 2 hours.	Greater than 10
Batch 1	Cooled using Freon-12.	5 minutes.	Ambient.	Approximately 2 hours.	Greater than 10
Batch 1	Cooled using Freon 12.	5 minutes.	Thawed in oven at 60°C.	3½ minutes.	Greater than 10
Batch 3	-25	28 minutes.	Thawed in oven at 60°C.	4 minutes.	4
Batch 3	-25	25 minutes.	Oven thawing.	3 minutes.	3
Batch 3	Cooled using Freon 12.	6 minutes.	Oven thawing.	4½ minutes.	3
Batch 3	Cooled using Freon 12.	5½ minutes.	Ambient.	Approximately 2 hours.	3

For Batch Details See Tables 4.1. and 4.9.

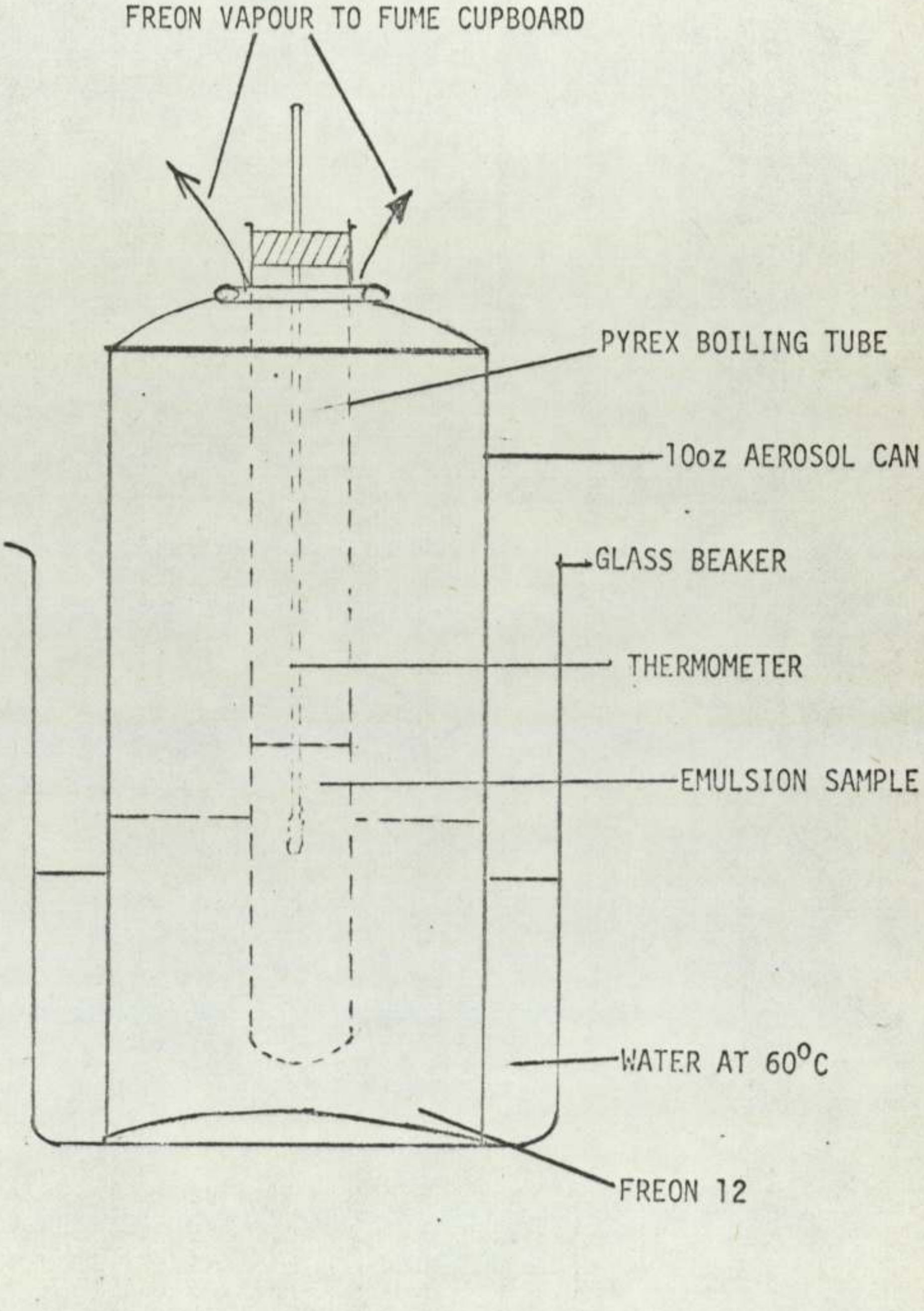
When the minute timer alarm bell sounded the samples were withdrawn from the freezer, checked for temperature and complete solidification then placed in a laboratory oven preset at 60^oC. (If the sample was not completely frozen it was returned to the freezer for a further time period). The minute timer was then reset to 4 minutes and when the samples had completed time in the oven, they were removed, checked for temperature and completeness of thaw. If the samples were unsatisfactory, they were returned to the oven, otherwise they were checked visually for changes in appearance after the completion of 1 cycle. If no significant changes in viscosity or appearance occurred, further cycles were pursued until changes described under 4.6.2. (b) occurred. The number of cycles completed to the point of change were then recorded and used as a measure of stability by comparison with a satisfactory product.

(ii). Using Freon 12.

Once again the test was conducted in duplicate by taking 25 ml samples in stoppered pyrex boiling tubes. The tubes, equipped with a thermometer, were in turn placed in an empty 10oz tinplate aerosol can part filled with Freon 12. The can was then placed in a beaker containing warm water inside a fume cupboard and the Freon allowed to evaporate freely. The refrigeration effect produced, rapidly cooled the emulsion to -1^oC in 3 to 5 minutes. The samples were then thawed in the oven as in (i) above and cycles repeated as necessary. The apparatus is illustrated in Figure 4.6.

FIG. 4.6.

APPARATUS FOR RAPID FREEZE THAW TECHNIQUE.



(f). Results.

The results of the experiments directed at establishing the test conditions for estimating wax emulsion stability by freeze/thaw cycling are presented in Table 4.18. The reproducibility of both methods is shown using the study emulsion and other wax emulsion products in Table 4.19. Comparisons with other test methods and conclusions are given in Section 4.7.

4.6.3. The Rapid Estimation of Wax Emulsion Stability by the Application of Destructive Forces.

The reason that freeze thaw cycling can be used to measure emulsion stability is that during the freezing cycle, the protective emulsifier layer around the wax particle(s) is disrupted as the phase change occurs. The electrical forces which hold the emulsion together are overcome by greater forces applied mostly by the water molecules changing to the solid phase.

The advantage of the freeze thaw method is that it can produce major changes in the emulsion appearance in a few hours, without departing too far from conditions that the emulsion may experience in normal use. However, often a really rapid result is required, as for example, in routine quality control. In such a situation, the only known recourse is to subject the sample to major disruptive forces such as electrical potential or extreme pH. The method used depends

TABLE 4.18. - DATA ON TIME OF FREEZE THAW CYCLES

SAMPLE REFERENCE		TIME IN FRIDGE OR OVEN IN MINUTES																									
		2	4	5	8	10	15	20	25	2ND CYCLE	2	4	5	8	10	15	20	25	3RD CYCLE	2	4	5	8	10	15	20	25
Batch 1	Sample temperature in fridge at -25°C in °C.	18		14		7	2	-½	-1		4				1	-½	-1			4	-	0	-	-½	-1		
	Sample temperature in oven at 60°C in °C	0	5								0	2	5							-½	4½						
Batch 3	Sample temperature in fridge at -25°C in °C	17	-			5	0	-½	-1		3		1		0		-½	-2		5					0	-½	-1½
	Sample temperature in oven at 60°C in °C	0	6								1	4	7							-½	3	6					

DEDUCED TEST CONDITIONS

Fridge Temperature = -25°C
Oven Temperature = +60°C
Solidification Temperature = -1°C (all sample is solid)
Thaw Temperature = 5°C (gives convenient time in oven)
Time for freeze down = 30 minutes
Time to thaw = 3 - 5 minutes

For Batch Details See Tables 4.1. and 4.9.

TABLE 4.19. - REPRODUCIBILITY OF FREEZE THAW TEST FOR WAX EMULSION STABILITY

SAMPLE BATCH REFERENCE	DETAILS OF BATCH*	NUMBER OF COMPLETE CYCLES TO APPEARANCE CHANGE	APPEARANCE CHANGE OBSERVED
Batch 1	Standard laboratory batch	Greater than 10	No real change.
Batch 1	Second sample	Greater than 10	No change.
Batch 3	Laboratory batch made with 50% of formula weight of emulsifier.	3	Loss of mobility.
Batch 3	Second sample	4	Loss of mobility.
Batch 3	Third sample	3	Loss of mobility.
Batch 5	Laboratory batch made with 10% of formula weight of alkali.	1	Heavy wax separation
Batch 5	Second sample	1	Heavy wax separation.
Batch 8	Laboratory batch made with 150% of formula weight of alkali.	2	Loss of mobility and translucency.
Batch 8	Second sample.	3	Loss of mobility and translucency.
Batch 163 ex works	Standard works sample.	Greater than 10	Loss of mobility.
Batch 163	Second sample.	Greater than 10	Loss of mobility.

*See also Tables 4.1. and 4.9.

greatly on the emulsion being tested and its response to the particular stimulus. Some wax emulsions are for example, quite stable to high and low pH but may separate rapidly under applied voltage.

Great care is also required in establishing correlations with stability in normal environments. It may be that a rapid and measureable response to abnormal stimuli such as low pH, could fail to yield a correlation with the shelf stabilities described in 4.3.2. In such a situation, the data would be of little use. In the case of the study emulsion however, it was possible to relate stability at high pH with ambient storage and freeze thaw cycling. However, low pH environment produced no change with the study emulsion. A rapid test for stability was devised and this is described below. The subject of stability measurement is discussed in Section 9.

Titration Method for the Rapid Estimation of Study Emulsion Stability.

(a). Theory.

When the study emulsion was subjected to high pH, it appeared that inversion occurred to give a highly viscous water in wax emulsion. This change was accentuated by heat and was quite sharp and therefore measureable. Improperly formed emulsions required only a few millilitres of normal Sodium Hydroxide to effect the change. Normal product usually required more than 25 mls of Sodium Hydroxide to cause the change. The quantity of alkali required was therefore used as a measure of the emulsion stability.

(b). Apparatus.

The equipment is relatively simple and consists of: a 50 ml graduated beaker; thermometer (0-100^{0}C); variable speed magnetic stirrer; plastic coated stirrer bar; and normal sodium hydroxide solution contained in a 50 ml burette.

(c). Method.

25 ml of sample were raised to 60^{0}C then, with stirrer bar added and revolving at approximately 2 r.p.m., it was titrated with normal sodium hydroxide solution until the viscosity rose to the point where all mobility was lost. This point was usually sharply defined when the stirrer bar ceased to revolve. The time to complete this test was found to be approximately 5 minutes.

(d). Results.

The results obtained using the titration method with study emulsion are presented in Table 4.20. Comparisons and conclusions are presented in Section 4.7.

TABLE 4.20. - TITRATION METHOD FOR WAX EMULSION STABILITY

SAMPLE BATCH REFERENCE	MILLILITRE OF 1 N NaoH SOLUTION TO PRODUCE LOSS OF MOBILITY	COMMENTS
1	25.1	Standard laboratory quality.
2	23.2	Standard laboratory quality.
3	9.4	Made with 50% of formula weight of emulsion therefore stability should be reduced.
4	7.8	Made with 50% of formula weight of emulsion therefore stability should be reduced.
5	18.3	Made with only 10% of formula weight of alkali, stability should be therefore reduced. The method fails to induce a marked visible change i.e. loss of mobility.
6	14.8	Made with only 10% of formula weight of alkali, stability should be therefore reduced. The method fails to induce a marked visible change i.e. loss of mobility.
7	3.5	Though very fine emulsions, their stability as judged by the method is very low.
8	4.2	Though very fine emulsions, their stability as judged by this method is very low.
Batch 163 ex works	19.7	Standard quality product. Comparable with the stability standard laboratory batches.

For Batch Details See Tables 4.1. and 4.9.

4.7. Comparisons between Existing and Newly Developed Techniques for Assessing Wax Emulsion Performance (Stability).

The results obtained with the methods reviewed are presented for comparison in Table 4.21 for batches of the study emulsion 1 to 8. As stated earlier, ambient storage gives meaningful information but only after several months. This method should be regarded as absolute in terms of stability measurement and used as the basis for any correlation studies. Accelerated storage testing seems to provide more information for finished products which have marginal stability, than for wax emulsion intermediates. Any visual information that the test might yield will tend to be related to creaming tendency and is likely to take a long time to obtain. It was therefore not chosen for this project and is not recommended for wax emulsions.

Centrifugal testing only appears to be capable of assessing the tendency to form a cream layer and cannot be used to assess stability of the study emulsion in the sense of wax particulate aggregation, coalescence or inversion. As shown in Table 4.21. however, it was not really possible to rank study emulsion stabilities by the centrifuge method. Even the measurement of the depth of centrifuged wax or cream seemed to be subject to variations, perhaps due to different packing densities. As these cream layers were very small, little comparative information could be gained from them. Previous industrial experience suggested that a method incorporating a standard laboratory centrifuge was only likely to be useful if the

TABLE 4.21. - RESULTS OF STABILITY DETERMINATIONS BY DIFFERENT METHODS AND QUALITY RANKING (1> 10)

BATCH REFERENCE	1 YEAR AMBIENT STORAGE RESULT	RANKING	24 HOUR ACCELERATED STORAGE RESULT	RANKING	CENTRIFUGE RESULT	RANKING	FREEZE THAW RESULTS	RANKING	FAST FREEZE THAW RESULTS	RANKING	TITRATION RESULTS	RANKING
1	No cream	(1)	1mm cream	(2)	1mm cream	(2)	>10 cycles	(1)	>10 cycles	(1)	25.1mls	(1)
2	1mm cream	(3)	No cream	(1)	1mm cream	(2)	>10 cycles	(1)	>10 cycles	(1)	23.2mls	(2)
3	25mm cream	(4)	3mm cream	(3)	2mm cream	(3)	3-4 cycles	(3)	3-4 cycles	(3)	9.4mls	(7)
4	45mm cream	(5)	5mm cream	(5)	3mm cream	(3)	4 cycles	(2)	4 cycles	(2)	7.8mls	(8)
5	Complete Separation	(8)	4mm cream	(4)	14mm cream	(4)	1 cycle	(6)	1 cycle	(6)	18.3mls	(5)
6	Complete Separation	(8)	4mm cream	(4)	16mm cream	(5)	1 cycle	(6)	1 cycle	(6)	14.8mls	(6)
7	Viscosity increase	(6)	No cream	(1)	No cream	(1)	2 cycles	(5)	2 cycles	(5)	3.5mls	(10)
8	Gelled Completely	(7)	No cream	(1)	No cream	(1)	2-3 cycles	(4)	2-3 cycles	(4)	4.2mls	(9)
9	1mm cream	(3)	1mm cream	(2)	1mm cream	(2)	>10 cycles	(1)	>10 cycles	(1)	21.7mls	(4)
10	½mm cream	(2)	No cream	(1)	1mm cream	(2)	>10 cycles	(1)	>10 cycles	(1)	22.6mls	(3)

emulsion had very limited stability. As most batches of the study emulsion appeared to have relatively high stability, the method was rejected as being too insensitive. Nevertheless, it is likely that the use of a centrifuge capable of much higher speeds could be used to assess wax emulsion stability.

Freeze/thaw test results obtained from study emulsion batches 1-10 are also given in Table 4.21. which shows that both freezing methods yield substantially the same result and the choice is based on user convenience. If a really rapid result is required, the Freon 12 method would be chosen which enables 6 cycles to be completed in 1 hour. It would however demand all of the operators time for that hour. The freezer method would take 3½ hours to complete six cycles and 35 minutes to effect 1 cycle (compared with 10 minutes for the Freon method). However, the operator would be free to perform other tesks during the freezing part of the cycle. The minimum number of cycles required for the study emulsion to be assessed as satisfactory is 5. For some emulsions however, the control may be set as low as 3. Any emulsion completing 10 cycles will prove satisfactory in use. The actual number of cycles ideally needs determining for each emulsion, but a rough guide is 5 cycles.

Whichever freezing method is used, Table 4.21. illustrates that a ranking of emulsion stability is possible which appears to correlate with ambient testing. It is therefore recommended for the assessment of wax emulsion stability and will be used in this study.

Titration tests for stability are also shown in Table 4.21. and correlations with freeze/thaw methods and ambient storage are apparent. This is the fastest method of all but probably the one with the most limited applicability. Many wax emulsions would not give a sharp and measureable response to the addition of alkali and each emulsion requires careful evaluation against both freeze/thaw data and ambient storage data. In view of the correlations obtained both with ambient storage and freeze/thaw measurements, it could be used for stability assessment in this project.

4.8. Conclusions.

The criteria of a wax emulsion quality are appearance and performance.

Appearance.

(a) Wax emulsion appearance may be assessed by measuring the size of the disperse phase particles.

(b) While it is very difficult and time consuming to obtain a particle size distribution for most wax emulsions, their tendency to form a creamy layer (on storage) may be measured by the gravimetric test detailed in 4.4.4.

(c) Both particle counting and microscopic methods are unsuitable for conducting a particle size analysis on the study emulsion and probably on wax emulsions in general.

(d) If a particle size analysis is to be completed on a wax emulsion, centrifugal sedimentometry should be investigated.

(e) The changes in the submicron 'mother liquor' constituent of a wax emulsion and their bearing on emulsion appearance, may be conveniently monitored by light transmission techniques.

Performance.

(f) Wax emulsion performance may, for all practical purposes, be equated with wax emulsion stability. Hence the assessment of wax emulsion performance may be conveniently achieved by measuring stability.

(g) The freeze thaw technique detailed in Section 4.6.2. is the best way of measuring wax emulsion stability and hence performance.

(h) Centrifugation with a laboratory centrifuge (i.e. speeds up to 4000 rpm) may be useful for wax emulsions having low stability. However, it is likely that an ultra centrifuge could be used for all emulsions.

5. INVESTIGATION OF WAX EMULSIFICATION VARIABLES

5.1. Introduction.

Wax emulsions have been processed for many years and the factors controlling emulsion quality appear to have been established. However, there seems to be a need to optimise these factors in order that the number of unsatisfactory batches may be reduced and the general quality of wax emulsions improved. Further, it should be possible by optimising the processing variables, to simplify the equipment necessary to produce the wax emulsions. At the present time, there still appears to be a large "skill" factor associated with each industrial batch such that unsatisfactory results are often blamed on "lack of experience". This is a situation that need not arise if there is a greater understanding of the emulsification process particularly with regard to those factors which control quality. Once this understanding is achieved, there should be few obstacles remaining to complete process control.

5.2. Conclusions from Literature Review.

During the literature review, it was found that little work had been documented specifically dealing with wax emulsions. The reported variables are presented in Table 5.1., together with the importance assigned to them by various investigators. Other parameters likely to influence the wax emulsion product are also included.

TABLE 5.1 WAX EMULSIFICATION - IDENTIFIED SYSTEM VARIABLES

	Ranking of Important with Respect to Product Quality according to various investigators 1>2>3>4>5				
Variable Name	Lange	Hackett	Johnson & Draper	Bridgewater & Roberts	Comments
Emulsifier Level (a) Surface active agent (b) Free alkali	Not examined	1	1	1	
Wax Temperature	2		2	5	
Water Temperature	Unimportant			2	
Degree of Agitation of Water	Unimportant	2	4	3	
Wax Addition Rate	3	Not rated	3	4	
Rate of Cooling	4	Not rated	5	Not rated	
Melting Time	1	Not rated	Not rated	Not rated	
Water Hardness	5	Not rated	Not rated	Not rated	
Order of Addition of Reagents	Not rated	Not rated	Not rated	Not rated	
Acid Value of Wax	Not mentioned	Not mentioned	Not mentioned	Not rated	Acid value known (76) to be a measure of readiness to form emulsion
Saponification Time					Found to be of importance during this study.
Degree of Agitation of Wax Melt	Not mentioned	Not mentioned	Not mentioned	Not rated	Found to be of importance during this study.

As may be seen from Table 5.1., twelve variables have been identified, although their relative importance, in terms of producing a satisfactory emulsion, appear to be debateable.

5.3. Experimental Work Programme - Design of Experiments.

From the literature survey (Section 2) and the early experimental work conducted with the study emulsion (detailed in Sections 3 and 4), the system variables were identified and partially ranked by the time the detailed work programme was ready to start. Four major variables emerged; emulsifier level; degree of saponification; extent of agitation during emulsification and wax addition rate. The main experimental programme was set out to confirm and quantify these preliminary results and conduct some optimisation studies. The number of batches required to achieve this was estimated and considered to be acceptable in terms of necessary experimentations. Therefore a systematic approach was adopted rather than one involving a factorial or other statistically based experimental programme.

With the benefit of hindsight, this decision may be considered to be in error, for it is likely that if more time had been devoted to designing the programme of experiments aimed at studying the system variables, a small nett saving in time may have been possible. Due to the complexities in designing a suitable programme and the lack of understanding of interaction between variables at the time of instigation of the experimentation, the traditional approach was considered justified.

5.4. Description of Apparatus.

The apparatus required to investigate the emulsification variables has already been selected in Section 3.2. This equipment is illustrated in Plate 5.1. and a detailed specification is presented in Table 5.2. This may be useful in specification of a test procedure (See Section 7.3). In addition to the illustrated apparatus, a portable tachometer was used to determine agitator shaft speeds and the equipment described in Section 4 for quality assessment of the finished wax emulsion.

5.5. Experimental Techniques Used.

5.5.1. Establishment of a Data Base.

Preliminary consideration of the twelve identified variables indicated that some of these might be interdependent. For example, it was likely that the rate at which the molten wax was added would be related to the degree of agitation applied to the emulsion water. Therefore, before any evaluation aimed at ranking the importance of these variables could begin, it was considered necessary to define a set of 'standard' conditions. This was achieved by running preliminary experiments on the test apparatus in order to produce a wax emulsion of similar quality to that produced in industrial practice. A further constraint on the standard

PLATE 5.1.

Laboratory Emulsification Apparatus

TABLE 5.2. - EMULSIFICATION APPARATUS - SPECIFICATION

ITEM	SPECIFICATION	PURPOSE
Heating Mantle	Isomantle (1000 ml capacity) 300W	Emulsion vessel heater.
Heating Mantle	Isomantle (600 ml capacity) 200W	Wax Melt vessel heater.
Variable Speed Agitator	Heidolph Type 745 125W - 90 - 1800 rpm	Emulsion vessel.
Variable Speed Agitator	Premier 62 Variable Speed 100W	Wax melt vessel.
Tachometer	Smiths Venture Model ATH 4	Measurement of stirrer shaft speeds.
Emulsion Vessel	1 Litre squat glass beaker ID = 10cms Liquid Height = 5cms	Emulsification vessel,
Wax Melt Vessel	600ml squat beaker ID = 8½cms Liquid Height = 3cms Distance of propeller from base = 2cms	Wax melting and saponification vessel.

conditions was that they had to be capable of producing a constant quality product with the same raw materials.

In practice similar wax and water temperatures to those used in industry were used, while the minimum addition rate of wax to water was adjusted to be consistent with continuous addition of 83 grams of wax which is the quantity required to produce 500 grams of finished product. Other variables such as degree of agitation, rate of cooling and saponification time were fixed by repeated trials. The 'standard' conditions are summarised in Table 5.3.

5.5.2. Method of Investigation.

As described in Section 5.3., a systematic approach was then adopted whereby each variable was considered in turn, and its effect on product quality examined while the others were held constant. Later some of the more important variables were altered simultaneously, in attempts to produce data which would either define the extent of their influence on product quality, or their range of useful values. The techniques used for specific variables are described in more detail below and the methods for assessing product quality (% wax greater than 10 mM.; % light transmission; freeze/thaw studies) in Section 4.

5.5.3. Effect of Order and Mode of Addition of Reagents.

TABLE 5.3. STANDARD CONDITIONS FOR THE PRODUCTION OF THE STUDY EMULSION

Saponification Time = 5 minutes.

Wax Temperature = 120 - 130^{o}C.

Water Temperature = 95 - 98^{o}C.

Type of Agitator (emulsion vessel) = 3 bladed propelled 2:1 pitch.

Agitator Speed = 1000 r.p.m.

Type of Agitator (wax vessel) = 3 bladed propeller 2:1

Agitation Speed = 1200 r.p.m.

Wax Addition Rate = 52 - 53 g/min.

Melting Time = 10 minutes.

Acid Value of Wax = 40.

Cooling Rate based on batch size of 500g = 7^{o}C/min.

Water Hardness = 200 ppm of $CaCo_3$.

STUDY EMULSION FORMULA		% BY WEIGHT
AC540 Polyethylene Wax	=	16.59
Linear Ethoxylated Alcohol Emulsifier	=	3.11
Alkali (50% w/w)	=	0.60
Melt viscosity reductant (Ethylene Glycol)	=	0.85
Mains Water	=	78.85

Technique.

The standard conditions defined above were largely based on industrial practice. Therefore, the order of reagent addition followed the same procedure used frequently by industry. However, a series of experiments were run to investigate if this factor had any importance with regard to product quality.

In the initial series of experiments, wax only was melted and the viscosity checked at various temperatures by Brookfield viscometer (133). Ethylene Glycol, the melt viscosity reductant, was then added and after appropriate stirring, the viscosity remeasured. The standard quantity of potassium hydroxide was then added and the viscosity remeasured.

Using a fresh batch of wax, the viscosity was determined as melted and after emulsifier addition. Then potassium hydroxide was added and the viscosity remeasured. Finally, using a third batch of wax, viscosity was measured before and after potassium hydroxide addition. The results are presented in sheet R1.

The next series of runs were conducted with potassium hydroxide being added to the melted wax before and after the emulsifier. Three runs were made of each condition, (with glycol removed from the formula), plus a standard run for comparison. Finally, experiments were conducted with the alkali and emulsifier added to the emulsification water.

These results are shown in sheets R2 and R3.

DATA SHEET R1 - VISCOSITY OF WAX MELT

Composition of Wax Melt	Temp. ^{o}C	VISCOSITY OF BATCH BY BROOKFIELD VISCOMETER				Comments
		Spindle	Speed	Reading	Viscosity cps.	
Wax only	184 150 125	2 2 2	60 60 60	62 84 98	310 420 490	
Wax and Glycol	125 148	2 2	60 60	95 79	475 395	
Wax and Glycol and KOH	148 130	2 2	12 12	38 42	950) 1050)	Large viscosity increase probably due to formation of w/o emulsion and saponification reaction.
Wax only	130	2	60	95	475	
Wax and Tergitol	128	2	60	68	340	Substantial good reduction in viscosity.
Wax and Tergitol and KOH	128	2	12	25	625	Viscosity increase still present but depressed due to Tergitol.
Wax only	135	2	60	92	460	
Wax + KOH immediately after KOH addition.	134	2	12	40	1000	Very viscous toffee-like mass.
Wax + KOH 2 mins. after KOH addition.	133	2	12	32	800)	Viscosity dropped as water evaporated. Also wax mass changed from opaque mass to clear melt.
Wax + KOH 4 mins. after KOH addition.	134	2	12	28	700)	

RESULTS

VARIABLE(S) STUDIED **Order of Addition**

DATA SHEET NO R2

BATCH NUMBERS

Values of Other System Variables	12	13	14	15	16	17	18
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	135	140	125	128	134	127	133
Water T_w °C	94	96	95	94	96	96	92
Finished Emulsion T_e °C	90	93	91	92	95	94	90
Wax Processing							
Melting Time - mins	12	11	10	12	11.5	10	12
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	43	36	37	45	40	39	42
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	19.45	18.3	20.2	21.3	20.6	27.7	20.8
% Light Transmission	38	36	37	40	37.5	38	40.5
% Residue greater than 10mM	0.220	0.230	0.200	0.197	0.230	0.243	0.179
pH	10.0	10.1	9.9	10	10.1	9.95	10
Freeze/Thaw Cycles							
Comments Order of Additions to Wax.	1. KOH 2. Tergitol	1. KOH 2. Tergitol	1. Glycol 2. Tergitol 3. KOH	1. KOH 2. Tergitol	1. Tergitol 2. KOH	1. Tergitol 2. KOH	1. Tergitol 2. KOH

RESULTS

VARIABLE(S) STUDIED Order of Addition

DATA SHEET NO R3

BATCH NUMBERS

Values of Other System Variables	19	20	21	22	23		
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100		
KOH % w/w of formula weight	100	100	100	100	100		
Process Temperatures							
Wax Melt T_m °C	145	140	125	128	145		
Water T_w °C	93	95	92	94	98		
Finished Emulsion T_e °C	93	93	90	92	96		
Wax Processing							
Melting Time - mins	10	12	12	10	14		
Saponification Time - mins	5	5	5	5	5		
Addition Rate g/min	43	45	38	36	47		
Cooling rate for emulsion °C/min	7	7	7	7	7		
Quality Assessment							
Non Volatile Content of Emulsion	Not measured due to complete separation	Complete separation	17.6	18.4	19.2		
% Light Transmission			0	0	0		
% Residue greater than 10mM			53.5	38.5	33.7		
pH		12.9	10.1	10.2	9.95		
Freeze/Thaw Cycles							
Comments Order of Additions to Wax.	1. Tergitol 2. KOH in water	1. Tergitol 2. KOH in water	1. KOH 2. Tergitol in water	1. KOH 2. Tergitol in water	1. KOH 2. Tergitol in water		

Discussion.

The experiments conducted in Section 5.5.3. show that the order of addition of the reagents to the wax melt is unimportant in terms of product quality. However, the early addition of the surfactant will reduce the melt viscosity which reaches a peak following the addition of alkali. This peak is lowered by the presence of the formula weight of emulsifier. The ethylene glycol seems to have little effect on melt viscosity in comparison with the emulsifier, and its use was discontinued from this point. The use of alkali and/or emulsifier in the aqueous phase proved to be unsatisfactory.

5.5.4. The Effect of Emulsifier Levels.

Experimental Techniques.

From the completion of the preliminary work of this study, it became evident that with the selected emulsion, two emulsifying agents were present. It was also deduced that neither one would function satisfactorily without the presence of the other. For clarity they will be referred to as the surface active agent or 'emulsifier' (Tergitol 15-S-9 nonionic ethoxylated linear alcohol); and 'free alkali', namely 50% w/w potassium hydroxide solution. Much of the suppliers literature (76) tended to indicate that the important constituents of a wax emulsion were the wax itself and the emulsifier, namely the surface active agent. However, because the preliminary work indicated the importance of the alkali, both the materials were varied first independently and then simultaneously.

Experiments were conducted using otherwise standard conditions but decreasing emulsifier level such that batches were prepared containing 90%; 75% and 50% of the formula weight of emulsifier (See Table 5.3.).

The wax emulsion product obtained at 50% of the formula weight of tergitol was so unsatisfactory that no further reductions were attempted. Further batches were then prepared at 110%; 125%; 150%; 200%; 220%; 230%; 250%; 300%; and 350% of the formula weight. The results of these tests are shown in data Sheets R4, R5 and R6 and graphically in Figure 5.1.

RESULTS

VARIABLE(S) STUDIED = Emulsifier Level

DATA SHEET NO R4

BATCH NUMBERS

Values of Other System Variables	24	25	26	27	28	29	30
Emulsifiers							
Tergitol % w/w of formula wt.	100	90	75	65	50	50	100
KOH % w/w of formula wt.	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	122	140	123	140	124	130	151
Water T_w °C	95	96	95	95	97	96	94
Finished Emulsion T_e °C	92	94	91	92	95	94	92
Wax Processing							
Melting Time - mins	10	11	10	11	12	10	10
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	52	52.5	53	53	53	52.5
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	18.30	20.90	19.10	19.46	15.25	16.130	19.61
% Light Transmission	39.50	36.50	13	1	0	0	36.40
% Residue greater than 10mM	0.200	0.250	0.390	1.250	25.120	21.45	0.199
pH	9.75	9.85	9.80	9.9	9.85	9.8	9.85
Freeze/Thaw Cycles	>10	>10	8	4	3	3	>10
Comments	Standard Quality	Satisfactory product	Opaque unsatisfactory product	Opaque unsatisfactory product	Unsatisfactory	Unsatisfactory	Standard quality

RESULTS

VARIABLE(S) STUDIED = **Emulsifier Level**

DATA SHEET NO R5

BATCH NUMBERS

Values of Other System Variables	31	32	33	34	35	36	37
Emulsifiers							
Tergitol % w/w **of formula wt.**	110	125	150	200	220	220	230
KOH % w/w **of formula wt.**	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m ^{o}C	150	128	122	130	123	125	135
Water T_w ^{o}C	93	94	95	95	95	93	98
Finished Emulsion T_e ^{o}C	91	91	91	93	94	91	96
Wax Processing							
Melting Time - mins	11	10	11	11	10	10	10
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	52.5	53	53	53	53	52.5
Cooling rate for emulsion $^{o}C/min$	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	18.50	19.60	21.30	20.90	20.20	19.10	19.93
% Light Transmission	50.50	62	71	80	78	83	79
% Residue greater than 10mM	0.205	0.185	0.169	0.155	0.150	0.147	0.148
pH	9.7	9.8	9.8	9.85	9.8	9.8	9.85
Freeze/Thaw Cycles	>10	>10	>10	>10	>10	>10	>10
Comments	Good product	Good product	Excellent translucency	Excellent translucency	Excellent translucency	Excellent translucency	Excellent translucency

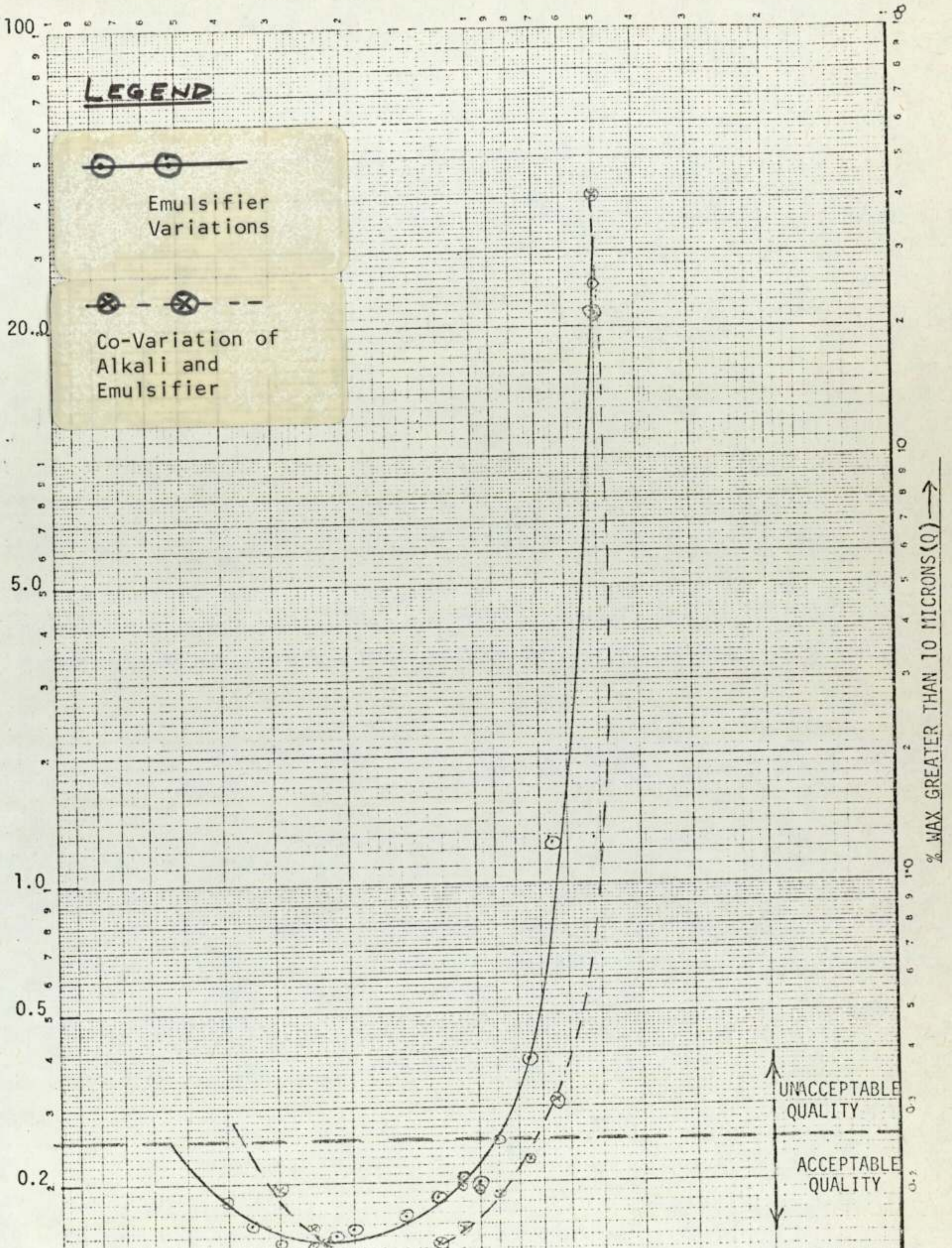
RESULTS

VARIABLE(S) STUDIED = Emulsifier Level

DATA SHEET NO R6

	BATCH NUMBERS						
Values of Other System Variables	38	39	40	41	42		
Emulsifiers							
Tergitol % w/w of formula weight	250	300	350	400	400		
KOH % w/w of formula weight	100	100	100	100	100		
Process Temperatures							
Wax Melt T_m ^oC	145	125	128	131	130		
Water T_w ^oC	95	94	93	94	95		
Finished Emulsion T_e ^oC	93	91	91	92	93		
Wax Processing							
Melting Time - mins	12	11	12	11	10		
Saponification Time - mins	5	5	5	5	5		
Addition Rate g/min	53	53	53	53	53		
Cooling rate for emulsion ^oC/min	7	7	7	7	7		
Quality Assessment							
Non Volatile Content of Emulsion	21.0	18.8	19.70	18.65	19.82		
% Light Transmission	74	63	55	61	58		
% Residue greater than 10mM	0.144	0.145	0.160	0.180	0.190		
pH	9.9	9.8	9.75	9.8	9.8		
Freeze/Thaw Cycles	>10	>10	>10	>10	>10		
Comments	Heavy foaming during emulsification	Foaming during emulsification	Heavy foaming	Heavy foaming	Heavy foam formed		

FIGURE 5.1. - VARIATION OF EMULSIFIER LEVEL



Discussion.

The variation of emulsifier levels in the wax melt proved to have considerable effects on emulsion quality when measured by the new quality control methods described in Section 4. Only small reductions in emulsifier could be tolerated without major reduction in product quality. Alternatively, wax emulsion translucency could be improved by extra emulsifier without disadvantages other than increased cost of manufacture. There was however a limit to such improvements, because substantial emulsifier additions in excess of 200% of formula weight produced heavy foaming during manufacture. This foam layer inhibited efficient emulsification, caused translucency to fall, and the percentage of wax greater than 10 microns to increase. The stabilities of all batches made with extra emulsifier were high. Practical limits were from 75 to 230 percent of formula weight.

5.5.5. The Effect of Alkali Level.

Experimental Techniques.

The effect of varying the formula weight of potassium hydroxide was studied by similar variations in formula weight to those used for the emulsifier in 5.5.4. (above). These results are presented in data sheets R7, R8, R9 and in Figure 5.2.

RESULTS

VARIABLE(S) STUDIED = **Alkali Level**

DATA SHEET NO R7

BATCH NUMBERS

Values of Other System Variables	43	44	45	46	47	48	49
Emulsifiers							
Tergitol % w/w **of formula wt.**	100	100	100	100	100	100	100
KOH % w/w **of formula wt.**	100	110	125	125	150	175	200
Process Temperatures							
Wax Melt T_m °C	122	128	135	130	120	126	134
Water T_w °C	95	95	97	94	96	94	94
Finished Emulsion T_e °C	92	93	95	92	94	92	92
Wax Processing							
Melting Time - mins	11	10	10	10.5	11	11	12
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	18.30	20.4	21.3	19.8	19.4	18.1	17.9
% Light Transmission	39.50	45	56	53	71	74	85
% Residue greater than 10mM	0.205	0.185	0.165	0.159	0.148	0.141	0.149
pH	9.78	9.9	10.2	10.1	10.5	10.9	11.2
Freeze/Thaw Cycles	>10	>10	8	9	3	2	1
Comments	Standard quality	Good product	Stability reduced	Stability reduced	Excellent translucency poor stability	Unacceptable stability	Unacceptable stability

RESULTS

VARIABLE(S) STUDIED = **Alkali Level**

DATA SHEET NO R8

BATCH NUMBERS

Values of Other System Variables	50	51	52	53	54	55	56
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	225	250	300	300	90	80	75
Process Temperatures							
Wax Melt T_m °C	128	125	127	135	130	144	140
Water T_w °C	94	96	93	95	93	94	95
Finished Emulsion T_e °C	92	94	91	93	91	92	94
Wax Processing							
Melting Time - mins	10.5	11	11	11	11	11	11
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	52.5	53	53	53	53	52.5	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	19.3	18.1	17.7	16.9	18.9	17.6	18.06
% Light Transmission	70	55	0	0	28	43	13.90
% Residue greater than 10mM	0.180	0.250	5.106	3.105	0.230	0.210	0.305
pH	11.8	12.3	12.9	12.85	9.7	9.65	9.1
Freeze/Thaw Cycles	1	1	0	0	>10	>10	>10
Comments	Wax degrading yellow melt	Wax degrading yellow melt	Unacceptable gelled on cooling	Unacceptable gelled on cooling	Acceptable	Good	Unacceptable quality

RESULTS

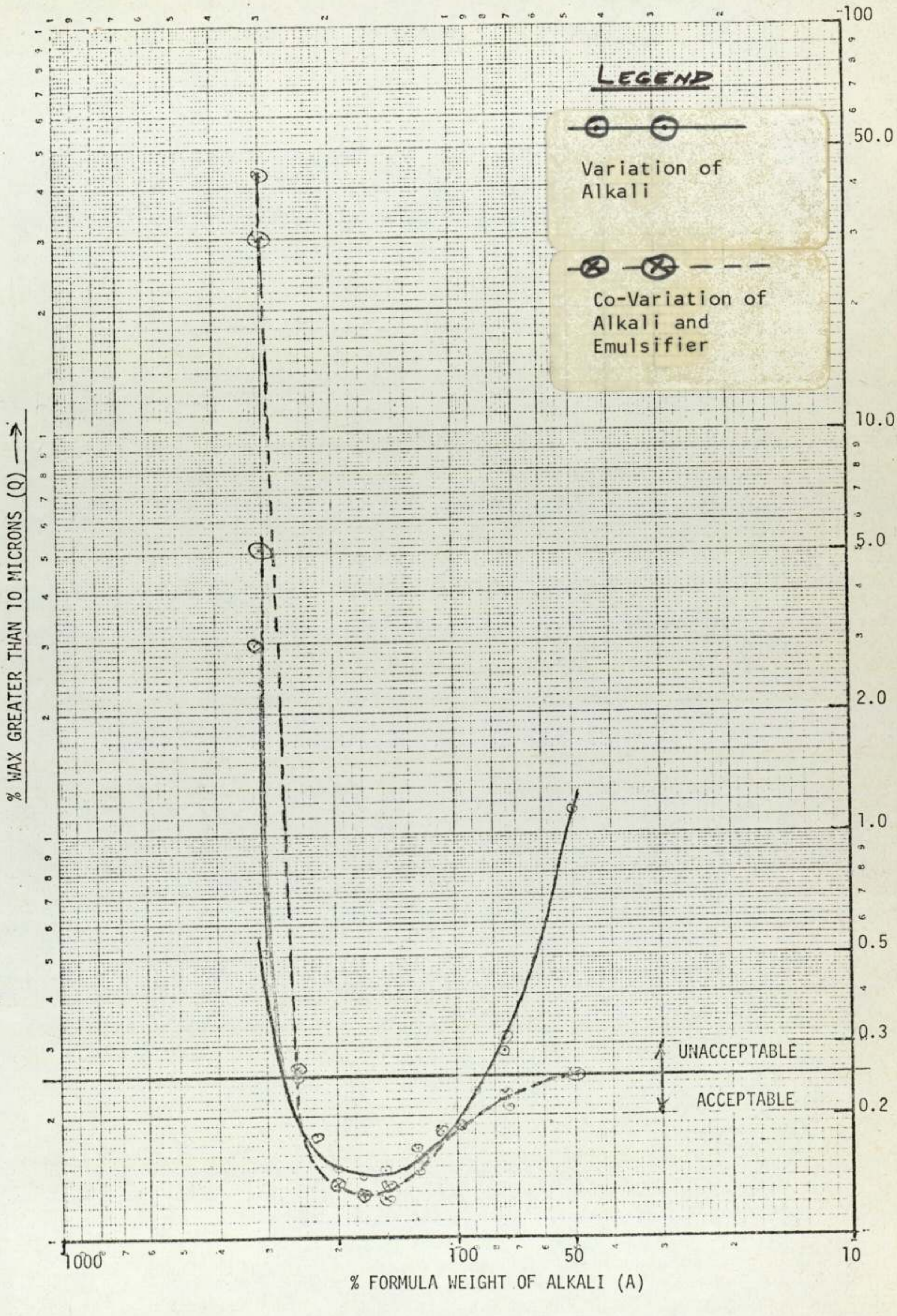
VARIABLE(S) STUDIED = Alkali Level

DATA SHEET NO R9

BATCH NUMBERS

Values of Other System Variables	57	58	59	60			
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100			
KOH % w/w of formula weight	75	50	0	0			
Process Temperatures							
Wax Melt T_m ^oC	128	150	164	128			
Water T_w ^oC	95	95	98	94			
Finished Emulsion T_e ^oC	93	94	96	93			
Wax Processing							
Melting Time - mins	10	10	11	10			
Saponification Time - mins	5	5	5	5			
Addition Rate g/min	53	53	53	53			
Cooling rate for emulsion $^oC/min$	7	7	7	7			
Quality Assessment							
Non Volatile Content of Emulsion	20.4	19.77					
% Light Transmission	10	2					
% Residue greater than 10mM	0.291	1.150	Not measured	Not measured			
pH	8.9	8.6					
Freeze/Thaw Cycles	>10	>10					
Comments	Unacceptable quality.	Unacceptable	Complete separation on cooling.	Complete separation on cooling.			

FIGURE 5.2. - VARIATION OF ALKALI LEVEL



Discussion.

Alkali variations produced similar effects on product translucency with the main difference that high levels of alkali reduced emulsion stability. Practical limits were established at 75 to 125% of formula weight. Higher values produced emulsions with unsatisfactory stability. Very high levels of alkali gave extreme discolouration and caused structural changes in the wax which inhibited its capability to be emulsified.

5.5.6. Co-variation of Emulsifier and Alkali.

Experimental Techniques.

This part of the work was completed by investigating the interdependence of the alkali and the Tergitol emulsifiers. During these experiments, first the alkali was held at 150% of the formula weight while the Tergitol level was taken through similar variations to before. This experiment was then re-run with the Tergitol level at 150% of the formula weight, while the alkali levels were varied. These results are shown in data sheets R10 to R13 and graphically in Figures 5.1. and 5.2.

VARIABLE(S) STUDIED = Covariations Emulsion/Alkali

RESULTS

DATA SHEET NO R10

BATCH NUMBERS

Values of Other System Variables	61	62	63	64	65	66	67
Emulsifiers							
Tergitol % w/w of formula weight	110	125	150	200	250	300	100
KOH % w/w of formula weight	150	150	150	150	150	150	150
Process Temperatures							
Wax Melt T_m °C	128	130	120	130	125	137	128
Water T_w °C	92	92	96	96	94	95	97
Finished Emulsion T_e °C	90	91	94	95	92	93	95
Wax Processing							
Melting Time - mins	12	11	10	10.5	11	11	10
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	52.5	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	19.1	20.2	20.3	23.4	18.7	17.8	19.3
% Light Transmission	77	83	89	86	83	40.5	65
% Residue greater than 10mM	0.159	0.148	0.130	0.135	0.158	0.195	0.161
pH	11.0	11.3	11.2	11.0	11.3	11.5	11
Freeze/Thaw Cycles	5	6	5	4	4	5	6
Comments	Translucency with reduced stability	Good translucency reduced stab.	Excellent translucency	Excellent translucency poor stability	Translucency falling	Heavy foaming during emulsification	Slightly reduced stability

VARIABLE(S) STUDIED = Covariations Emulsifier/Alkali

RESULTS

DATA SHEET NO R11

	BATCH NUMBERS						
Values of Other System Variables	68	69	70	71			
Emulsifiers							
Tergitol % w/w of formula weight	90	75	65	50			
KOH % w/w of formula weight	150	150	150	150			
Process Temperatures							
Wax Melt T_m ^oC	128	129	133	140			
Water T_w ^oC	95	98	96	96			
Finished Emulsion T_e ^oC	93	96	95	94			
Wax Processing							
Melting Time - mins	12	10	10.5	11			
Saponification Time - mins	5	5	5	5			
Addition Rate g/min	53	53	53	53			
Cooling rate for emulsion ^oC/min	7	7	7	7			
Quality Assessment							
Non Volatile Content of Emulsion	19.7	22.9	18.61	17.06			
% Light Transmission	60	30	5	0.9			
% Residue greater than 10mM	0.189	0.275	0.310	40.500			
pH	11.4	10.9	11.1	11.3			
Freeze/Thaw Cycles	5	4	2	1			
Comments	Reduced stability	Reduced stability	Unacceptable quality	Unacceptable quality			

RESULTS

VARIABLE(S) STUDIED = Covariations Alkali/Emulsifier

DATA SHEET NO R12

BATCH NUMBERS

Values of Other System Variables	72	73	74	75	76	77	78
Emulsifiers							
Tergitol % w/w of formula weight	150	150	150	150	150	150	150
KOH % w/w of formula weight	100	110	125	150	150	175	200
Process Temperatures							
Wax Melt T_m °C	122	125	132	120	124	121	138
Water T_w °C	94	95	93	96	93	95	95
Finished Emulsion T_e °C	91	93	92	94	91	92	93
Wax Processing							
Melting Time - mins	11	10.5	12	11	11	10	10.5
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	21.3	20.8	19.6	20.3	19.4	18.5	20.6
% Light Transmission	71	78	82	89	87	87.5	87
% Residue greater than 10mM	0.190	0.186	0.155	0.135	0.125	0.126	0.135
pH	9.8	9.9	10.5	11.3	11.1	11.2	11.6
Freeze/Thaw Cycles	>10	>10	9	5	4	2	1
Comments	Good translucency	Good translucency	Slight loss of stability	Good translucency poor stability	Good translucency poor stability	Poor stability	Poor stability

VARIABLE(S) STUDIED = Covariation Alkali/Emulsifier

RESULTS

DATA SHEET NO R13

BATCH NUMBERS

Values of Other System Variables	79	80	81	82	83	84	85
Emulsifiers							
Tergitol % w/w of formula weight	150	150	150	150	150	150	150
KOH % w/w of formula weight	250	300	300	90	75	75	50
Process Temperatures							
Wax Melt T_m °C	135	131	125	128	127	123	147
Water T_w °C	94	94	93	93	98	95	94
Finished Emulsion T_e °C	92	93	91	90	95	94	92
Wax Processing							
Melting Time - mins	11	10	10	11	10	11	12
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	18.9	20.1	18.6	19.3	21.9	17.9	20.8
% Light Transmission	65	0	0	60	49	45	13
% Residue greater than 10mM	0.260	43.501	30.050	0.209	0.225	0.219	0.250
pH	11.9	12.8	12.85	9.7	9.1	9.3	8.8
Freeze/Thaw Cycles	1	1	1	> 10	> 10	> 10	> 10
Comments	Totally unacceptable	Totally unacceptable	Totally unacceptable	Above standard quality	Standard quality	Standard quality	Barely acceptable

Discussion.

The highest translucency coincident with low values of unemulsified wax was achieved by increasing both emulsifier and alkali. This effect is illustrated in Figures 5.1. and 5.2. Nevertheless, these improvements are small compared with those achieved by the use of emulsifier alone. It should also be borne in mind that improvements in product translucency accomplished by the joint increase of alkali and emulsifier are probably achieved at the expense of product stability.

5.5.7. The Effect of Wax Saponification Time.

Experimental Techniques.

The suppliers literature (76) indicated that the alkali was present to saponify the wax. No mention was made of rate of reaction or the time required to effect its completion. Therefore experiments were made to determine if this variable was important. Using otherwise standard conditions, the time for saponification was varied from 10 seconds to several hours. In addition to the normal quality assessment tests already discussed in Section 4, the pH of the finished emulsions were recorded and compared with the theoretical pH produced using 3% by weight of 50% by weight potassium hydroxide solution in the formula. Without chemical reaction which would demand hydroxide, the theoretical pH would be 12.71. These results are presented in data sheets R14 and R15 and in Fig 5.3.

RESULTS

VARIABLE(S) STUDIED = Saponification Time

Wax agitator speed = 1900 rpm

DATA SHEET NO R14

BATCH NUMBERS

Values of Other System Variables	86	87	88	89	90	91	92
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	125	122	130	131	128	135	138
Water T_w °C	95	94	95	94	92	95	93
Finished Emulsion T_e °C	94	92	93	92	91	93	91
Wax Processing							
Melting Time - mins	12	11	11	10	10	11	10.5
Saponification Time - secs.	10	20	20	30	45	60	90
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	19.3	17.5	20.3	18.17	19.51	19.70	17.43
% Light Transmission	0	2	15	28.5	34	41	40
% Residue greater than 10mM	24.81	1.250	0.210	0.234	0.236	0.204	0.224
pH	12.3	11.6	11.0	10.2	10	10.1	10
Freeze/Thaw Cycles	>10	>10	>10	>10	>10	>10	>10
Comments	Opaque free wax	Opaque free wax	Poor translucency	Almost standard quality.	Standard quality	Standard quality	Standard quality

RESULTS

VARIABLE(S) STUDIED = Saponification Time

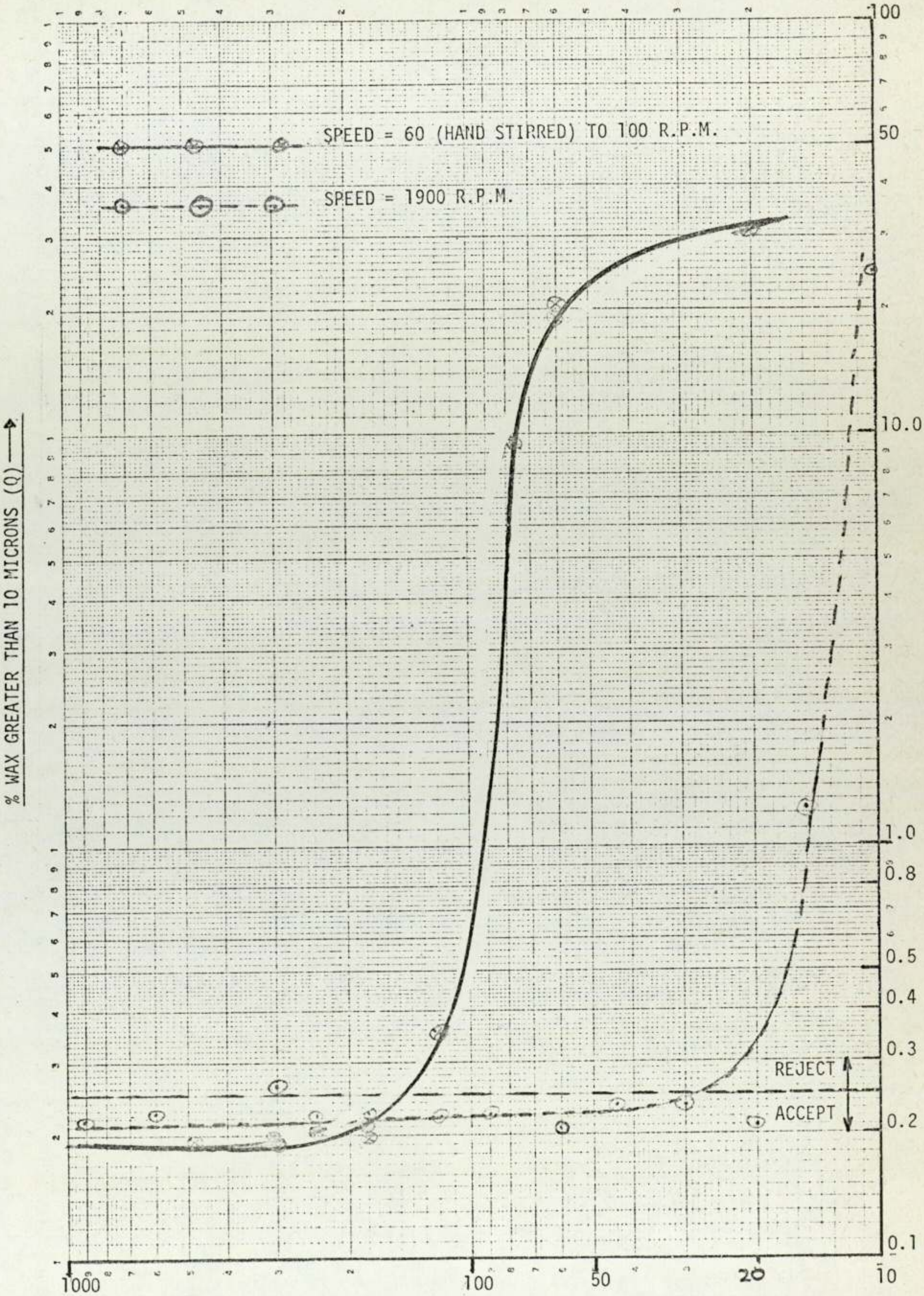
Wax agitator speed = 1900 rpm

DATA SHEET NO R15

BATCH NUMBERS

Values of Other System Variables	93	94	95	96	97	98	
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	
KOH % w/w of formula weight	100	100	100	100	100	100	
Process Temperatures							
Wax Melt T_m °C	140	125	120	125	121	134	
Water T_w °C	95	93	96	94	93	94	
Finished Emulsion T_e °C	93	91	95	92	91	92	
Wax Processing							
Melting Time - mins	12	10	10.5	12	11	10	
Saponification Time - mins	120	180"(3')	240"(4')	300"(5')	3600"(60')	25,200"(7hrs)	
Addition Rate g/min	53	53	53	53	53	53	
Cooling rate for emulsion °C/min	7	7	7	7	7	7	
Quality Assessment							
Non Volatile Content of Emulsion	17.36	18.71	21.25	19.63	20.11	18.33	
% Light Transmission	53	42	40.5	42	39	43.5	
% Residue greater than 10mM	0.223	0.227	0.225	0.265	0.240	0.235	
pH	9.8	9.9	9.8	9.75	9.9	9.85	
Freeze/Thaw Cycles	>10	>10	>10	>10	>10	>10	
Comments	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality	Yellow product due to hydrolysis	

FIGURE 5.3. - SAPONIFICATION TIME VERSUS Q.



SAPONIFICATION TIME IN SECONDS.

Discussion.

The level of alkali controls the translucency of wax emulsion to a marked extent but only if it has reacted with the wax. As shown in data sheet R2, the addition of alkali to the aqueous phase results in an unsatisfactory product.

The experiments aimed at establishing the importance of providing the right conditions for the reaction of alkali with molten wax are summarised in data sheets R15, R16 and Figure 5.3. Without full saponification, a poor quality product results. Unfortunately the (saponification) reaction of the alkali with the wax is accompanied by the release of water and a high viscosity melt due to the formation of water in oil emulsion. This viscosity peak occurs at the time when good agitation of the melt is required to assist the saponification reaction. The effect can be minimised by the presence of the emulsifier as shown in data sheet R1. Fortunately, with reasonably good agitation, the reaction is completed in 3 - 5 minutes.

The wax temperature appears to be unimportant in terms of the saponification reaction, (provided that the wax is molten), the controlling factor being the extent of agitation of the melt. However this is more fully investigated later.

5.5.8. The Degree of Agitation of the Wax Melt.

Experimental Techniques.

This was investigated next because the experiments conducted under 5.5.7. above, indicated that saponification time was related to the degree of wax agitation. Again using standard conditions, the saponification experiments conducted above were repeated with different rates of agitation of the wax melt. The results are presented in data sheets R16 and R17.

RESULTS

VARIABLE(S) STUDIED = Saponification Time

Wax agitation speed = 100 rpm

DATA SHEET NO R16

	BATCH NUMBERS						
Values of Other System Variables	99	100	101	102	103	104	105
Emulsifiers							
Tergitol % w/w of formula wt	100	100	100	100	100	100	100
KOH % w/w of formula wt	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	126	129	134	139	124	119	133
Water T_w °C	95	95	95	94	95	96	92
Finished Emulsion T_e °C	93	94	93	92	93	93	91
Wax Processing							
Melting Time - mins	11	10.5	11	12	11.5	10.5	10
Saponification Time secs.	10"	20"	60"	120"	180"	240"	300"
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	Not measured due to heavy separation	19.3	18.7	18.95	21.25	19.35	18.73
% Light Transmission		0	0	8	21	33	39.5
% Residue greater than 10mM		30.113	20.310	0.352	0.210	0.208	0.191
pH	12.6	12.3	12.1	10.5	9.9	9.8	9.9
Freeze/Thaw Cycles	Not measured	2	8	> 10	> 10	> 10	> 10
Comments	Little emulsification	Heavy wax separation	Heavy wax separation	Opaque unsatisfactory product.	Almost satisfactory	Standard quality	Standard quality

RESULTS

VARIABLE(S) STUDIED = Saponification Time

Wax Agitation speed = 60 rpm

DATA SHEET NO R17

BATCH NUMBERS

Values of Other System Variables	106	107	108	109			
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100			
KOH % w/w of formula weight	100	100	100	100			
Process Temperatures							
Wax Melt T_m °C	122	125	131	128			
Water T_w °C	96	93	94	92			
Finished Emulsion T_e °C	93	91	92	91			
Wax Processing							
Melting Time - mins	12	10	12	11			
Saponification Time - mins	1*	3*	5*	8*			
Addition Rate g/min	53	53	53	53			
Cooling rate for emulsion °C/min	7	7	7	7			
Quality Assessment							
Non Volatile Content of Emulsion	20.91	18.91	19.33	18.27			
% Light Transmission	0	25.1	32	39			
% Residue greater than 10mM	19.481	0.203	0.198	0.210			
pH	10.5	9.9	9.9	9.8			
Freeze/Thaw Cycles	9	>10	>10	>10			
Comments	Heavy wax separation	Standard quality	Standard quality	Standard quality			

*Hand stirred with thermometer @ approximately 60 rpm.

Discussion.

There is no doubt that the rate of saponification is proportional to the extent of agitation of the wax melt. As discussed earlier, for most wax melts, the melt temperature is sufficient to guarantee a rapid reaction providing good mixing is present. This facilitates water removal by evaporation which in turn encourages the rate and extent of saponification. This is well illustrated in Figure 5.3 The provision of good mixing conditions are hindered somewhat by the initial formation of a water in wax emulsion which is accompanied by a large viscosity increase. This situation is alleviated by water evaporation.

5.5.9. The Effect of Wax Temperature.

Experimental Techniques.

Previous knowledge indicated that wax melt temperature could be important for the following reasons:-

(a) It might effect the rate of saponification of the wax.

(b) The temperature must be sufficiently high to keep the wax molten and high wax temperatures may assist the production of satisfactory emulsion when water temperatures are low.

(c) At very high temperatures, degradation, discolouring or charing of the wax may occur.

(d) At very high wax temperatures, degradation or hydrolysis of the emulsifier may occur.

(a) The effect of wax temperature on the rate of saponification was observed during the experiments conducted under 5.5.7. However, further experiments were conducted during otherwise standard conditions during which the wax was allowed to saponify for thirty seconds, one minute, 1½ minutes, 2 minutes, and 5 minutes at wax temperatures ranging from 120°C up to 200°C. These results are presented in data sheets R18, R19 and R20.

(b) The effect of wax melt temperature (i.e. including emulsifiers) in terms of keeping the wax molten and mobile was then investigated by using temperatures varying from the drop point (135) up to 301°C and the results are presented in data sheets R21 and R22.

(c) Further experiments were conducted holding the wax alone at various temperatures for prolonged periods by observing changes. Emulsions were subsequently made by addition of emulsifier and alkali at the end of the holding period. These results are presented in data sheets R23 and R24.

(d) The effect of loss or hydrolysis of the emulsifier was investigated by using otherwise standard conditions and holding the wax melts for varying periods of time and observing changes, in both the melt itself and the resultant emulsion. Temperatures from 120^{o}C up to 200^{o}C were used for periods up to 8 hours and the results are presented in data sheets R25 and R26.

RESULTS

VARIABLE(S) STUDIED = Wax Melt Temperature
(effect on saponification)

DATA SHEET NO R18

	BATCH NUMBERS						
Values of Other System Variables	110	111	112	113	114	115	116
Emulsifiers							
Tergitol % w/w of formula wt	100	100	100	100	100	100	100
KOH % w/w of formula wt	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	120	150	200	121	153	202	119
Water T_w °C	94	96	95	96	95	93	94
Finished Emulsion T_e °C	92	93	92	93	93	92	92
Wax Processing							
Melting Time - mins	10.5	11	10	12	10	11	12
Saponification Time - mins	30 secs	30 secs	30 secs	1	1	1	1½
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	18.7	18.9	16.7	19.9	18.71	19.89	19.6
% Light Transmission	5	12	17	36	37.5	39.2	41
% Residue greater than 10mM	0.383	0.258	0.266	0.225	0.233	0.201	0.196
pH	10.5	10.6	10.4	9.9	10	9.8	9.9
Freeze/Thaw Cycles	> 10	> 10	> 10	> 10	> 10	> 10	> 10
Comments	Opaque product unacceptable	Opaque product unacceptable	Unacceptable	Standard quality	Standard quality	Standard quality	Standard quality

RESULTS

VARIABLE(S) STUDIED = Wax Melt Temperature
(effect on saponification)

DATA SHEET NO R19

BATCH NUMBERS

Values of Other System Variables	117	118	119	120	121	122	123
Emulsifiers							
Tergitol % w/w of formula wt	100	100	100	100	100	100	100
KOH % w/w of formula wt	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	150	198	120	153	206	118	155
Water T_w °C	94	95	95	92	95	94	97
Finished Emulsion T_e °C	93	93	92	91	93	92	94
Wax Processing							
Melting Time - mins	10	10	10	10.5	11	10.5	11
Saponification Time - mins	1½	1½	2	2	2	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	21.63	19.1	22.2	19.61	17.8	19.3	18.8
% Light Transmission	45	44	48	46	39	36.5	39.5
% Residue greater than 10mM	0.209	0.198	0.206	0.211	0.246	0.247	0.205
pH	9.9	9.9	10	10	9.8	9.9	9.9
Freeze/Thaw Cycles	> 10	> 10	> 10	> 10	> 10	> 10	> 10
Comments	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality

RESULTS

VARIABLE(S) STUDIED = Wax Melt Temperature (effect on saponification)

DATA SHEET NO R20

BATCH NUMBERS

Values of Other System Variables	124						
Emulsifiers							
Tergitol % w/w of formula wt	100						
KOH % w/w of formula wt	100						
Process Temperatures							
Wax Melt T_m °C	197						
Water T_w °C	93						
Finished Emulsion T_e °C	91						
Wax Processing							
Melting Time - mins	11						
Saponification Time - mins	5						
Addition Rate g/min	53						
Cooling rate for emulsion °C/min	7						
Quality Assessment							
Non Volatile Content of Emulsion	20.3						
% Light Transmission	40.2						
% Residue greater than 10mM	0.240						
pH	10						
Freeze/Thaw Cycles	$>$ 10						
Comments	Standard quality.						

RESULTS

VARIABLE(S) STUDIED = Wax Temperature
(Normal hold time)

DATA SHEET NO R21

BATCH NUMBERS

Values of Other System Variables	125	126	127	128	129	130	131
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	98	110	123	135	151	184	205
Water T_w °C	95	94	95	94	93	94	93
Finished Emulsion T_e °C	94	93	93	93	92	92	91
Wax Processing							
Melting Time - mins	10.5	11	11.5	11	10	10.5	11
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	23.4	22.6	20.6	17.06	18.12	17.7	18.95
% Light Transmission	22.5	38	37.5	39.5	42	39.5	46
% Residue greater than 10mM	20.217	0.213	0.233	0.212	0.197	0.189	0.196
pH	10.1	10	10	9.9	9.8	9.9	9.85
Freeze/Thaw Cycles	8	>10	>10	>10	>10	>10	>10
Comments	Heavy wax separation	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality

RESULTS

VARIABLE(S) STUDIED = Wax Temperature (Normal hold time)

DATA SHEET NO R22

BATCH NUMBERS

Values of Other System Variables	132	133	134				
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100				
KOH % w/w of formula weight	100	100	100				
Process Temperatures							
Wax Melt T_m ^oC	250	255	301				
Water T_w ^oC	94	93	95				
Finished Emulsion T_e ^oC	92	91	94				
Wax Processing							
Melting Time - mins	11	11.5	11				
Saponification Time - mins	5	5	5				
Addition Rate g/min	53	53	53				
Cooling rate for emulsion ^oC/min	7	7	7				
Quality Assessment							
Non Volatile Content of Emulsion	19.8	21.2	20.06				
% Light Transmission	35.5	41.7	42				
% Residue greater than 10mM	0.249	0.209	0.199				
pH	10	9.9	9.9				
Freeze/Thaw Cycles	>10	>10	>10				
Comments	Standard quality	Standard quality	Wax yellowing (hydrolysis).				

RESULTS

VARIABLE(S) STUDIED = Wax Temperature (Extended Hold of Wax only)

DATA SHEET NO R23

BATCH NUMBERS

Values of Other System Variables	135	136	137	138	139	140	141
Emulsifiers							
Tergitol % w/w of formula wt.	100	100	100	100	100	100	100
KOH % w/w of formula wt.	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	120	122	118	126	150	149	155
Water T_w °C	94	95	94	95	92	94	95
Finished Emulsion T_e °C	92	93	93	92	91	93	93
Wax Processing							
Melting Time - mins	60	120	240	480	60	120	240
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	24.1	19.3	21.6	19.6	18.7	19.93	23.2
% Light Transmission	39.5	40.7	41.9	39.5	36.3	44	40.1
% Residue greater than 10mM	0.207	0.212	0.179	0.188	0.227	0.206	0.236
pH	10	10	9.9	9.85	9.9	10	9.85
Freeze/Thaw Cycles	> 10	> 10	> 10	> 10	> 10	> 10	> 10
Comments	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality

RESULTS

VARIABLE(S) STUDIED = Wax Temperature
(Extended Hold of Wax Only)

DATA SHEET NO R24

BATCH NUMBERS

Values of Other System Variables	142	143	144	145	146		
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100		
KOH % w/w of formula weight	100	100	100	100	100		
Process Temperatures							
Wax Melt T_m °C	151	202	207	200	219		
Water T_w °C	94	95	94	95	95		
Finished Emulsion T_e °C	93	94	92	93	94		
Wax Processing							
Melting Time - mins	480	60	120	240	480		
Saponification Time - mins	5	5	5	5	5		
Addition Rate g/min	53	53	53	53	53		
Cooling rate for emulsion °C/min	7	7	7	7	7		
Quality Assessment							
Non Volatile Content of Emulsion	21.65	19.13	18.35	19.4	22.3		
% Light Transmission	38.5	41	39	40	44		
% Residue greater than 10mM	0.242	0.203	0.216	0.229	0.208		
pH	9.8	10	9.9	9.85	9.9		
Freeze/Thaw Cycles	>10	>10	>10	>10	>10		
Comments	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality		

RESULTS

VARIABLE(S) STUDIED = Wax Melt Temperature (Extended Hold Time)

DATA SHEET NO R25

BATCH NUMBERS

Values of Other System Variables	147	148	149	150	151	152	153
Emulsifiers							
Tergitol % w/w of formula wt.	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	125	123	119	124	150	150	151
Water T_w °C	95	96	97	92	97	94	93
Finished Emulsion T_e °C	93	93	96	91	95	92	91
Wax Processing							
Melting Time - mins	10	11	10	10	10	10	10
Saponification Time - mins	60	120	240	480	60	120	240
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	23.2	20.89	19.35	18.63	16.9	18.8	21.9
% Light Transmission	36.5	41	38.5	43	40	43.5	38.9
% Residue greater than 10mM	0.229	0.219	0.221	0.236	0.211	0.194	0.199
pH	10	9.9	9.9	10	9.9	9.85	10
Freeze/Thaw Cycles	>10	>10	>10	>10	>10	>10	>10
Comments	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality	Standard quality

RESULTS

VARIABLE(S) STUDIED = Wax Melt Temperature (Extended Hold Time)

DATA SHEET NO R 26

BATCH NUMBERS

Values of Other System Variables	154	155	156	157	158		
Emulsifiers							
Tergitol % w/w of formula wt.	100	100	100	100	100		
KOH % w/w of formula wt.	100	100	100	100	100		
Process Temperatures							
Wax Melt T_m °C	154	201	207	200	202		
Water T_w °C	98	95	94	95	94		
Finished Emulsion T_e °C	96	93	93	94	92		
Wax Processing							
Melting Time - mins	10	12	11	10.5	11		
Saponification Time - mins	480	60	120	240	480		
Addition Rate g/min	53	53	53	53	53		
Cooling rate for emulsion °C/min	7	7	7	7	7		
Quality Assessment							
Non Volatile Content of Emulsion	22.3	20.6	18.6	21.15	23.10		
% Light Transmission	43.7	42.2	38.7	36.3	30.7		
% Residue greater than 10mM	0.179	0.210	0.201	0.207	0.246		
pH	10	9.9	10	10	10		
Freeze/Thaw Cycles	> 10	> 10	> 10	> 10	> 10		
Comments	Standard quality	Slight yellowing	Slight yellowing	Considerable yellowing	Pronounced yellowing		

Discussion.

Assuming that the wax is fully molten, then it would seem that its temperature will be adequate to ensure the occurrence of saponification and subsequently, emulsification. Elevated temperatures seem to accelerate the oxidation and thermal degradation of the melt. These changes manifest themselves in the form of colour development and the loss of the ability to emulsify properly. A general rule used by the polish industry which suggests that melt temperatures should be 10 - 15^{o}C above the drop point seems to be adequate for most purposes.

5.5.10. The Effect of Water Temperature.

Experimental Techniques.

From the preliminary experiments conducted in Section 3, it was clear that if the emulsion water was too cold, an unsatisfactory emulsion would result. However, it was of interest to determine the lower limit of water temperature and to find out if a low water temperature could be compensated for by a high wax temperature.

Experiments were first run using otherwise standard conditions but starting with emulsification water at ambient (20^{o}C) temperature. The temperature was then increased in 10 degree increments until 70^{o}C was reached and thence in 5 degree increments. The results are presented in data sheets R27 and R28 and in Figures 5.4. and 5.5.

Similar experiments were then conducted using Beeswax as a substitute for AC 540 Polyethylene Wax in the study formula (See Table 5.3.) in order to investigate the critical temperature difference between wax and water. The results are presented in data sheets R29 and R30 and in Figures 5.4. and 5.5.

Using the study formula once more, the relationship between wax temperature and water temperature was investigated by depressing the water temperature below the already determined minimum limit (see above and R27) and attempting emulsification using high temperature wax. These results are presented in data sheets R31 and R32.

RESULTS

VARIABLE(S) STUDIED = Water Temperature

DATA SHEET NO R27

BATCH NUMBERS

Values of Other System Variables	159	160	161	162	163	164	165
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	125	131	140	133	125	140	120
Water T_w °C	20	30	40	52	60	76	81
Finished Emulsion T_e °C	32	35	51	59	66	82	85
Wax Processing							
Melting Time - mins	10	11	10	11	10	10.5	11
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	2.4	3	3.5	4.7	5.5	6	6.5
Quality Assessment							
Non Volatile Content of Emulsion	2.35	1.32	3.61	3.02	14.37	20.35	17.8
% Light Transmission	Not measured	Not measured	Not measured	Not measured	1.5	2.5	7
% Residue greater than 10mM	95.36	93.05	91.71	92.64	15.06	4.351	0.365
pH	8.1	7.9	8.3	8.3	10.2	9.9	9.8
Freeze/Thaw Cycles	Not measured	Not measured	Not measured	Not measured	>10	>10	>10
Comments	Little emulsification	Little emulsification	Little emulsification	Little emulsification	Very opaque	Opaque	Slight translucency

RESULTS

VARIABLE(S) STUDIED = Water Temperature

DATA SHEET NO R28

BATCH NUMBERS

Values of Other System Variables	166	167	168				
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100				
KOH % w/w of formula weight	100	100	100				
Process Temperatures							
Wax Melt T_m °C	150	140	128				
Water T_w °C	92	95	98				
Finished Emulsion T_e °C	90	93	96				
Wax Processing							
Melting Time - mins	11	11	11.5				
Saponification Time - mins	5	5	5				
Addition Rate g/min	53	53	53				
Cooling rate for emulsion °C/min	7	7	7				
Quality Assessment							
Non Volatile Content of Emulsion	18.5	19.9	23.2				
% Light Transmission	33.5	43.7	39				
% Residue greater than 10mM	0.195	0.197	0.205				
pH	9.9	9.9	10				
Freeze/Thaw Cycles	>10	>10	>10				
Comments	Standard quality	Standard quality	Standard quality				

RESULTS

VARIABLE(S) STUDIED = WATER TEMPERATURE
BEESWAX EMULSION

DATA SHEET NO R29

BEESWAX EMULSION

BATCH NUMBERS

Values of Other System Variables	169	170	171	172	173	174	175
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	70	81	73	88	80	90	74
Water T_w °C	15	30	40	50	55	60.5	63
Finished Emulsion T_e °C	32	34	47	56	58	65	68
Wax Processing							
Melting Time - mins	10	10	10	10	10	10	10
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	Not Cooled	Not Cooled	4	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	18.14	19.37	15.571	19.190	20.141	17.644	16.189
% Light Transmission	Not measured	Not measured	Not measured	Not measured	Not measured	Not measured	Not measured
% Residue greater than 10mM	58.104	28.430	4.752	0.120	0.108	0.150	0.149
pH	Not measured	Not measured	Not measured	Not measured	Not measured	Not measured	Not measured
Freeze/Thaw Cycles	Not measured	Not measured	Not measured	Not measured	Not measured	Not measured	Not measured
Comments	← Little Emulsification Occurred →			Good Emulsion	Good Emulsion	Good Emulsion	Good Emulsion

RESULTS

VARIABLE(S) STUDIED = WATER TEMPERATURE

DATA SHEET NO R30

BEESWAX EMULSION

BATCH NUMBERS

Values of Other System Variables	176	177	178				
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100				
KOH % w/w of formula weight	100	100	100				
Process Temperatures							
Wax Melt T_m °C	87	74	85				
Water T_w °C	41	39.5	34				
Finished Emulsion T_e °C	49	43	41				
Wax Processing							
Melting Time - mins	10	10	10				
Saponification Time - mins	5	5	5				
Addition Rate g/min	53	53	53				
Cooling rate for emulsion °C/min	5	4.5	Not Cooled				
Quality Assessment							
Non Volatile Content of Emulsion	17.56	18.32	16.58				
% Light Transmission	Not measured	Not measured	Not measured				
% Residue greater than 10mM	0.215	2.091	15.010				
pH	Not measured	Not measured	Not measured				
Freeze/Thaw Cycles	Not measured	Not measured	Not measured				
Comments	Poor Emulsion Free Wax	Poor Emulsion Free Wax	Little Emulsification				

RESULTS

VARIABLE(S) STUDIED = Covariation of Wax and Water Temperatures

DATA SHEET NO R31

BATCH NUMBERS

Values of Other System Variables	179	180	181	182	183	184	185
Emulsifiers							
Tergitol % w/w of formula wt	100	100	100	100	100	100	100
KOH % w/w of formula wt	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	125	140	201	225	129	143	207
Water T_w °C	75	77	74	76	85	84	85
Finished Emulsion T_e °C	77	80	80	82	84	86	86
Wax Processing							
Melting Time - mins	10	10.5	11	11	11	11.5	11
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	19.8	21.1	19.13	19.7	18.9	19.61	21.3
% Light Transmission	1.2	1	1.5	6	8	15	12
% Residue greater than 10mM	3.55	4.01	2.87	0.401	0.316	0.287	0.303
pH	10	10.1	9.9	9.9	9.8	9.8	9.9
Freeze/Thaw Cycles	>10	>10	>10	>10	9	>10	>10
Comments	Opaque product	Opaque product	Opaque product	Opaque product	Opaque product	Opaque product	Opaque product

RESULTS

VARIABLE(S) STUDIED = Covariation of Wax and Water Temperatures

DATA SHEET NO R32

BATCH NUMBERS

Values of Other System Variables	186	187	188				
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100				
KOH % w/w of formula weight	100	100	100				
Process Temperatures							
Wax Melt T_m °C	127	203	110				
Water T_w °C	90	91	90				
Finished Emulsion T_e °C	92	91.5	89				
Wax Processing							
Melting Time - mins	11	10	10				
Saponification Time - mins	5	5	5				
Addition Rate g/min	53	53	53				
Cooling rate for emulsion °C/min	7	7	7				
Quality Assessment							
Non Volatile Content of Emulsion	20.9	19.3	18.6				
% Light Transmission	38.5	41	39.5				
% Residue greater than 10mM	0.216	0.203	0.244				
pH	9.9	9.9	9.9				
Freeze/Thaw Cycles	>10	>10	>10				
Comments	Standard quality	Standard quality	Standard quality				

FIGURE 5.4. - QUALITY Q VERSUS TEMPERATURE DIFFERENCE BETWEEN WAX & WATER

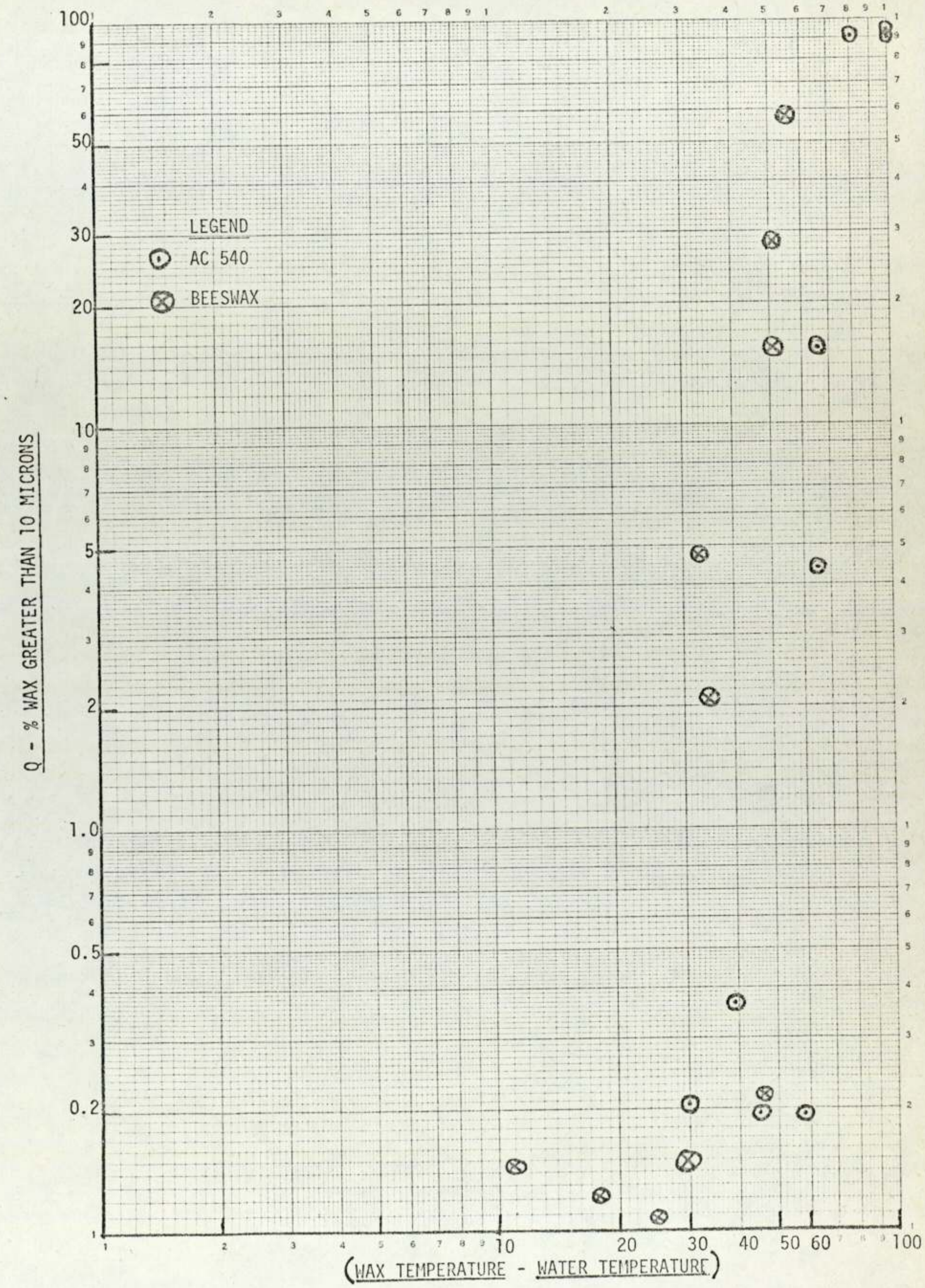
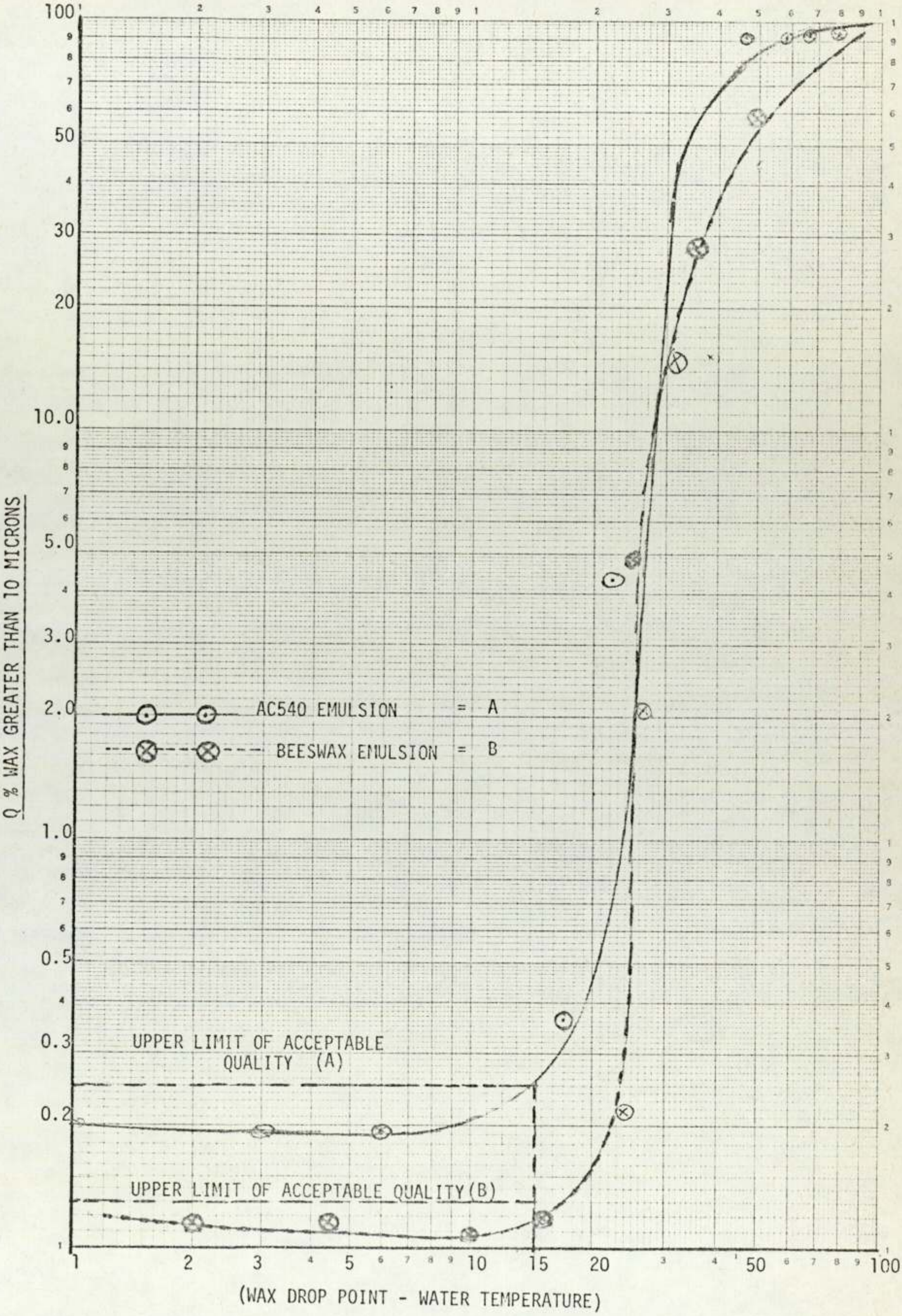


FIGURE 5.5. - VARIATION OF DIFFERENTIAL TEMPERATURE



Discussion.

The water temperature variations are presented in data sheets R27 and R28, in Figures 5.4. and 5.5. for the study emulsion. Further data gathered with the Beeswax formula is shown in sheets R29 and R30 and in Figures 5.4. and 5.5. These results show that the maximum temperature difference between the wax drop point and the water that can be tolerated for a successful emulsion is 15°C. This in turn means that it is not possible to process wax melts with drop points in excess of 110°C (assuming standard process conditions). As a general rule, water temperature should therefore be held as high as possible within the limits of control. It is detrimental to product quality for the water to boil and thus a temperature of 95°C is preferred because it takes account of the temperature rise due to the addition of hot (approximately 120°C) wax. In addition, there is no advantage in using cold or cool water with the exception of a slight energy saving. The use of water which is too cold cannot be counteracted by the use of high temperature (i.e. greater than 130°C) wax, and this is demonstrated via the batches in data sheets R31 and R32. This is because the critical factor is wax solidification which relates only to the wax drop point temperature. In the case of the study emulsion, this is 98°C and at this point, the wax solidifies. Therefore, the absolute minimum water temperature must be 83°C, otherwise the wax stream will partially or totally solidify on contacting the water. Even if the outer skin of the stream starts to solidify, the effect on emulsification will be marked. The wax will not form droplets as efficiently as in the molten state and an unsatisfactory emulsion will almost certainly result. The drop point of the Beeswax melt was found to be 65°C.

5.5.11. The Effect of Agitation on Emulsification Water.

Experimental Techniques.

Previous experience of industrial practice indicated that the degree of agitation during emulsification was a very important factor. During the design stage, the test rig was based on commercial wax emulsification practice and kept as simple as possible with a propeller agitator and wax addition to the water surface. No aids to efficient mixing such as baffles, draught tubes or special agitators were initially incorporated because of the intention to keep close to current industrial practice. The main considerations during this section were:-

(a) Variation in existing (propeller type) agitator rpm.
(b) Variation of type and diameter of agitator.
(c) Application of baffles.

From other experiments conducted in Section 3, it was clear that the agitator had two main functions. The first being to draw wax into the aqueous media and prevent it from lying on the water surface where it would cool and solidify, thereby making emulsification impossible. The second function was to apply sufficient shear to the molten wax stream to cause its disintegration into microscopic and sub-microscopic particles. The former effects were studied in this Section and the formation of the micro/submicroscopic particles in Section 6.4.6..

In the first series of experiments, standard conditions were maintained except that agitator rpm was varied from 250 rpm up to the machine maximum of 1500 rpm. These results are presented in data sheets R33 and R34 and in Figure 5.6.

The "down draught" effect of the various agitators in relation to submerging the molten wax stream was studied using dyed wax for easy observation. The objective of this exercise was to establish the relationship between a particular agitator speed and wax feed rate. Measurements were made (relevant to agitator rpm), of the feed rate which produced solid (cooled) wax on the water surface. This feed rate was referred to as the 'overload' feed rate and was considered important with respect to the agitator system. As stated previously, the cooled solidified wax would not emulsify resulting in an unsatisfactory product. The results of these experiments are presented in data sheets R35 in Fig.5.7.

Further experiments were conducted with solid wax dice as normally supplied by the wax manufacturer. These experiments were undertaken in order to investigate the down draught effect of various agitator types. A typical wax feed rate was chosen of 0.9 gms/sec (equivalent to a total addition time of 2 minutes), and 0.9 grams of wax was added to normal quantity of water for emulsification (See Section 3). The speed required to totally submerge this quantity of wax was then determined for each type of agitator in order to assess the suitability of the agitation system for making a wax emulsion to the standard formula and process. These results are shown in data sheets R36 and R37.

Experiments were then completed to confirm the results obtained with wax dice by making emulsions to the standard process except for varying stirrer speeds. During these tests, the agitator speeds previously shown to be capable of submerging the 0.9g of wax were utilised and the results are presented in data Sheets R38 and R39.

VARIABLE(S) STUDIED = EXTENT OF WATER AGITATION

RESULTS

DATA SHEET NO R33

BATCH NUMBERS

Values of Other System Variables	189	190	191	192	193	194	195
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m ^oC	128	143	140	134	134	145	144
Water T_w ^oC	95	96	95	94	93	95	93
Finished Emulsion T_e ^oC	94	93	96	96	96	97	95
Wax Processing							
Melting Time - mins	10	10	10.5	11	10	11	11
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion ^oC/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	20.3	21.45	19.90	21.23	19.65	22.13	19.71
% Light Transmission	44	39	40	42	38	36	22
% Residue greater than 10mM	0.190	0.210	0.218	0.202	0.215	0.241	0.247
pH	9.8	9.8	9.9	9.9	9.8	9.9	9.9
Freeze/Thaw Cycles	>10	>10	>10	>10	>10	>10	>10
Comments	1500 rpm. machine max. speed.	1000 rpm.	750 rpm.	750 rpm.	500 rpm.	500 rpm.	350 rpm.

RESULTS

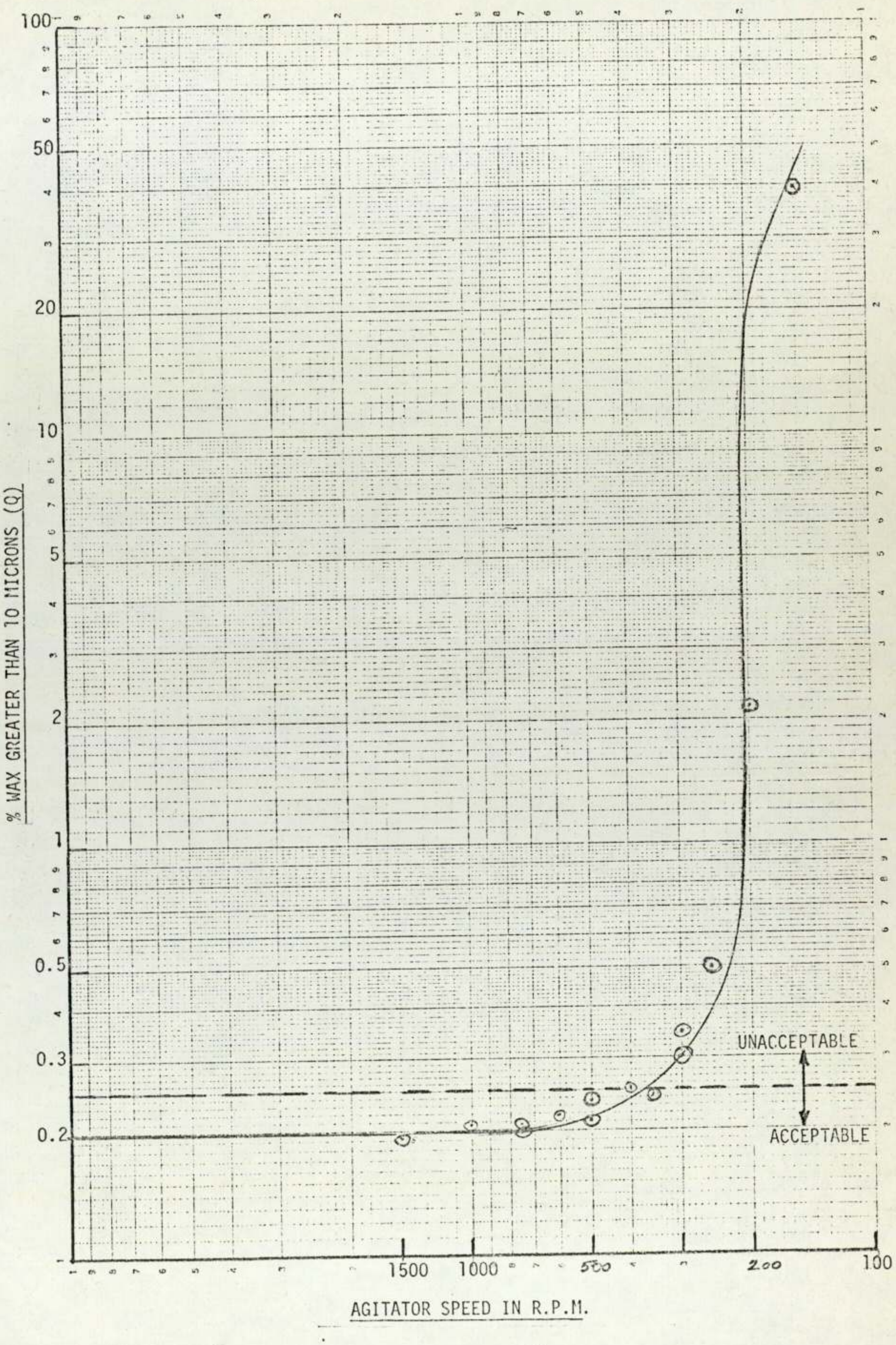
VARIABLE(S) STUDIED = EXTENT OF WATER AGITATION

DATA SHEET NO R34

BATCH NUMBERS

Values of Other System Variables	196	197	198	199	200	201	202
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	130	141	131	128	134	127	135
Water T_w °C	95	94	95	93	96	93	94
Finished Emulsion T_e °C	96	95	94	94	97	94	96
Wax Processing							
Melting Time - mins	10	10	10.5	12	11	11	10
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	16.47	17.13	19.87	18.76	15.44	wax failed to submerge or emulsify	wax failed to submerge or emulsify
% Light Transmission	20	15	18	21	40.5		
% Residue greater than 10mM	0.349	0.300	0.505	2.150	39.542		
pH	9.8	9.8	9.75	9.8	9.8		
Freeze/Thaw Cycles	>10	>10	>10	>10	>10		
Comments	300 rpm.	300 rpm.	250 rpm.	200 rpm.	150 rpm.	100 rpm.	100 rpm.

FIGURE 5.6. - RELATION BETWEEN AGITATOR SPEED AND EMULSION QUALITY



DATA SHEET R35

WAX FEED RATES PRODUCING THE OVERLOAD CONDITION

AGITATOR SPEED	WAX ADDITION TIME SECS.	ADDITION RATE g/MIN	VISUAL EFFECTS
1500	5.9	1075	None.
1000	5.9	1075	Wax building up on water surface and water boiling.
500	10.0	1057	Wax overload. Water boiling.
500	20.0	423	No overload.
350	20.0	423	Heavy overload. Water boiling.
350	30.0	211	Wax overload.
350	60.0	106	No overload.
300	60.0	106	Heavy overload.
300	120.0	53	Heavy overload.
300	240.0	27	Heavy overload.
300	598.0	10.6	Heavy overload.

DATA SHEET R36 - DOWNTHRUST EFFECT OF AGITATORS

TYPE OF AGITATOR	SPEED R.P.M.	BAFFLES	OBSERVATIONS
Standard 3 blade marine propeller. Diameter = 45mm.	100	None	Wax moving but not all submerged.
	200	None	Wax moving but not all submerged.
	300	None	Wax moving but not all submerged.
	400	None	All wax submerged and in suspension.
Standard 3 blade as above.	100	4 at 90°C 10% of vessel diameter.	Wax moving but not completely submerged.
	200	4 at 90°C 10% of vessel diameter.	Wax moving but not completely submerged.
	300	4 at 90°C 10% of vessel diameter.	Wax moving but not completely submerged.
	350	4 at 90°C 10% of vessel diameter.	Wax completely submerged and in suspension.
Small flat paddle (diameter = 17.5mm)	100	None	Wax hardly moving. All on surface.
	200	None	Wax hardly moving. All on surface.
	400	None	Wax moving but not all submerged.
	500	None	Wax moving but not all submerged.
	600	None	Wax moving but not all submerged.
	700	None	All wax submerged and in suspension.
Small flat paddle as above i.e. 17.5mm diameter.	100	4 at 90°C 10% of vessel diameter.	Wax moving and submerging to an increasing extent as speed increases but some wax still present on water surface.
	900	4 at 90°C 10% of vessel diameter.	Wax moving and submerging to an increasing extent as speed increases but some wax still present on water surface.
	1000	4 at 90°C 10% of vessel diameter.	All wax submerged and in suspension.

DATA SHEET R37 - DOWNTHRUST EFFECT OF AGITATORS

TYPE OF AGITATOR	SPEED R.P.M.	BAFFLES	OBSERVATIONS
Small pitched paddle (diameter = 17.5mm) (pitch = 2/1)	100 to 1200	None	Wax moving and submerging to an increasing extent as speed increases but some wax present on water surface.
	1300	None	All wax submerged and in suspension.
Small pitched paddle as above.	1500	4 at 90°C 10% of vessel diameter.	All wax submerged and in suspension. At speeds less than 1500 r.p.m., some wax permanently on water surface.
Large pitched paddle (diameter = 95mm) (pitch = 2/1)	250	None	Minimum speed to submerge 0.9g wax = 250
Flat turbine (diameter = 30mm) (4 blades at 90°C)	400	None	All wax submerged and in suspension,
Flat turbine as above.	500	4 at 90°C 10% of vessel diameter.	All wax submerged and in suspension.

RESULTS

VARIABLE(S) STUDIED = TYPE OF AGITATOR

DATA SHEET NO R38

	BATCH NUMBERS						
Values of Other System Variables	203	204	205	206	207	208	209
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	126	130	122	132	131	121	140
Water T_w °C	94	96	93	96	94	96	95
Finished Emulsion T_e °C	93	97	94	97	95	94	93
Wax Processing							
Melting Time - mins	10	11	10	10	10	10	10
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	20.2	19.6	18.8	19.6	17.9	21.0	19.6
% Light Transmission	39	30.5	28	33	35	28	32
% Residue greater than 10mM	0.247	0.261	0.271	0.239	0.222	0.299	0.321
pH	9.75	9.8	9.8	9.8	9.9	9.8	9.8
Freeze/Thaw Cycles	>10	>10	>10	>10	>10	>10	>10
Comments	Std.agitator 400 rpm.	Std.agitator 400 rpm. Baffles	Small Flat paddle 700rpm.	Small Flat paddle 1000 rpm.4 Baffles	Small pitched paddle 1300 rpm.	Small pitched paddle & Baffles 1500 rpm.	Large pitched paddle 250rpm.

RESULTS

VARIABLE(S) STUDIED = TYPE OF AGITATOR

DATA SHEET NO R39

BATCH NUMBERS

Values of Other System Variables	210	211					
Emulsifiers							
Tergitol % w/w of formula weight	100	100					
KOH % w/w of formula weight	100	100					
Process Temperatures							
Wax Melt T_m ^oC	125	133					
Water T_w ^oC	94	97					
Finished Emulsion T_e ^oC	95	98					
Wax Processing							
Melting Time - mins	10	11					
Saponification Time - mins	5	5					
Addition Rate g/min	53	53					
Cooling rate for emulsion ^oC/min	7	7					
Quality Assessment							
Non Volatile Content of Emulsion	18.1	19.6					
% Light Transmission	40.5	38					
% Residue greater than 10mM	0.286	0.207					
pH	9.8	9.8					
Freeze/Thaw Cycles	>10	>10					
Comments	Turbine 400 rpm.	Turbine 500 rpm.4 Baffles					

Discussion.

The importance of the water agitator can be deduced from data sheets which also give an indication of the performance of the various types of agitator. The experimental results show how the agitator must provide downthrust to draw the molten wax stream into the bulk of the aqueous medium otherwise an overload condition exists. The other major effect of the agitator, namely to cause droplet formation is dealt with in Section 6. Returning to the Concept of downthrust, a correlation should be possible between the theoretically calculated total force generated by the agitator and the force required to submerge the incoming wax stream at a given feed rate. This exercise is completed in Section 5.6. Using the laboratory apparatus, it was not possible to make a satisfactory emulsion below 350 r.p.m. due to inadequate downthrust, causing the wax to build up on the water surface and to overcool prior to emulsification. Although an emulsion still formed under these circumstances, it contained a large quantity of unemulsified wax fragments which yielded an unacceptable cream layer on standing.

5.5.12. Effect of Wax Addition Rate.

Experimental Techniques.

As described in the previous section, wax addition rate is related to the degree of agitation of the emulsification water. As discussed in Section 3, the standard conditions were set with reference to the maximum values of wax addition likely to be encountered during industrial practice. However, with the laboratory apparatus, it was not possible to duplicate such addition rates in terms of mass flow per second. Therefore simulation was effected on the basis of linear velocity. For example, a typical industrial plant was observed to transport molten wax for emulsification through a 7½cm pipe at a velocity of 26cm sec^{-1}. The standard addition rate of wax on the laboratory apparatus was 52.9g/min or 57.7 cm^3/min via a 2mm diameter stream. This corresponds to a linear velocity of 30cm sec^{-1} i.e. comparable with the industrial flow velocity. The limiting factor appeared to be the high viscosity of the wax melt in relation to typical pipe diameters used for molten wax transportation from melt vessel to emulsion water. Previous experience indicated that there are few examples where molten wax is pumped to emulsification vessel, the usual practice being to feed by gravity.

Therefore a series of experiments were conducted using otherwise standard conditions but varying additon rates and agitator speeds. This was most conveniently achieved by hand pouring and the use of a stop watch. Addition rates varying between 976 grams per minute down to 35 grams per minute were used. Speeds varied between 300 rpm. and 1,000 rpm. and results of these experiments are presented in data sheets R40 to R44 and in Figure 5.7.

RESULTS

VARIABLE(S) STUDIED = COVARIATION OF AGITATOR SPEED AND WAX FEED RATE

DATA SHEET NO R40

BATCH NUMBERS

Values of Other System Variables	212	213	214	215	216	217	218
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	125	140	128	121	133	140	129
Water T_w °C	94	95	96	94	95	96	93
Finished Emulsion T_e °C	98	97	97	93	91	94	90
Wax Processing							
Melting Time - mins	10.5	11	10	10	11	10.5	11
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	976	634	317	211	106	53	35
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	17.46	19.32	18.76	19.14	20.02	18.73	19.51
% Light Transmission	34	38	40	38	41	39	36
% Residue greater than 10mM	0.265	0.195	0.188	0.191	0.189	0.192	0.186
pH	9.8	9.9	9.8	9.8	9.8	9.9	9.8
Freeze/Thaw Cycles	>10	>10	>10	>10	>10	>10	>10
Comments O/L = Overload	1000 rpm. slight O/L	1000 rpm No O/L	1000 rpm. No O/L	1000 rpm. No O/L	1000 rpm. No O/L	1000 rpm. No O/L	1000 rpm. No O/L

RESULTS

VARIABLE(S) STUDIED = COVARIATION OF AGITATOR SPEED AND WAX FEED RATE

DATA SHEET NO R 41

BATCH NUMBERS

Values of Other System Variables	219	220	221	222	223	224	225
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	127	133	126	137	122	124	129
Water T_w °C	93	95	93	95	94	95	94
Finished Emulsion T_e °C	95	96	91	94	93	93	92
Wax Processing							
Melting Time - mins	11	11	10	11	10	11	10.5
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	976	634	317	211	106	53	35
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	18.79	22.10	19.38	20.41	20.68	19.91	21.33
% Light Transmission	30	40	37	39	40	41	36
% Residue greater than 10mM	0.295	0.215	0.201	0.205	0.210	0.199	0.203
pH	9.8	9.9	9.8	9.8	9.9	9.9	9.8
Freeze/Thaw Cycles	>10	>10	>10	>10	>10	>10	>10
Comments O/L = Overload	750 rpm. O/L	750 rpm. No O/L	750 rpm. No O/L	750 rpm. No O/L	750 rpm. No O/L	750 rpm. No O/L	750 rpm. No O/L

<u>VARIABLE(S) STUDIED</u> = COVARIATION OF AGITATION SPEED AND WAX FEED RATE

RESULTS

DATA SHEET NO R42

BATCH NUMBERS

Values of Other System Variables	226	227	228	229	230	231	232
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	122	131	129	135	132	125	126
Water T_w °C	94	96	94	94	93	94	92
Finished Emulsion T_e °C	95	97	93	92	91	92	90
Wax Processing							
Melting Time - mins	10	11	10	11	10	10	11
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	976	634	317	211	106	53	35
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	18.72	21.42	19.27	21.38	17.79	19.61	21.71
% Light Transmission	28	35	37	36	38	36.5	39
% Residue greater than 10mM	0.495	0.245	0.210	0.213	0.217	0.214	0.208
pH	9.8	9.8	9.8	9.8	9.9	9.8	9.8
Freeze/Thaw Cycles	>10	>10	>10	>10	>10	>10	>10
Comments	500 rpm. O/L	500 rpm. No O/L	500 rpm. No O/L	500 rpm. No O/L	500 rpm. No O/L	500 rpm. No O/L	500 rpm. No O/L

RESULTS

VARIABLE(S) STUDIED = COVARIATION OF AGITATOR SPEED AND WAX FEED RATE

DATA SHEET NO R43

BATCH NUMBERS

Values of Other System Variables	233	234	235	236	237	238	239
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	121	125	132	128	130	124	136
Water T_w °C	94	94	94	93	95	92	95
Finished Emulsion T_e °C	98	96	95	91	93	90	92
Wax Processing							
Melting Time - mins	10	10	11	10	10	11	11
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	976	634	317	211	106	53	35
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	Complete	14.16	18.49	19.83	20.64	21.33	20.11
% Light Transmission	Overload	Not measured	2	19	31	36	38
% Residue greater than 10mM	No quality	81.611	30.100	0.475	0.248	0.225	0.221
pH	parameters	8.2	9.7	9.8	9.9	9.8	9.8
Freeze/Thaw Cycles	measured	Not measured	7	> 10	> 10	> 10	> 10
Comments	350 rpm. O/L	350 rpm. O/L	350 rpm. O/L	350 rpm. O/L	350 rpm. Slight O/L	350 rpm. No O/L	350 rpm. No O/L

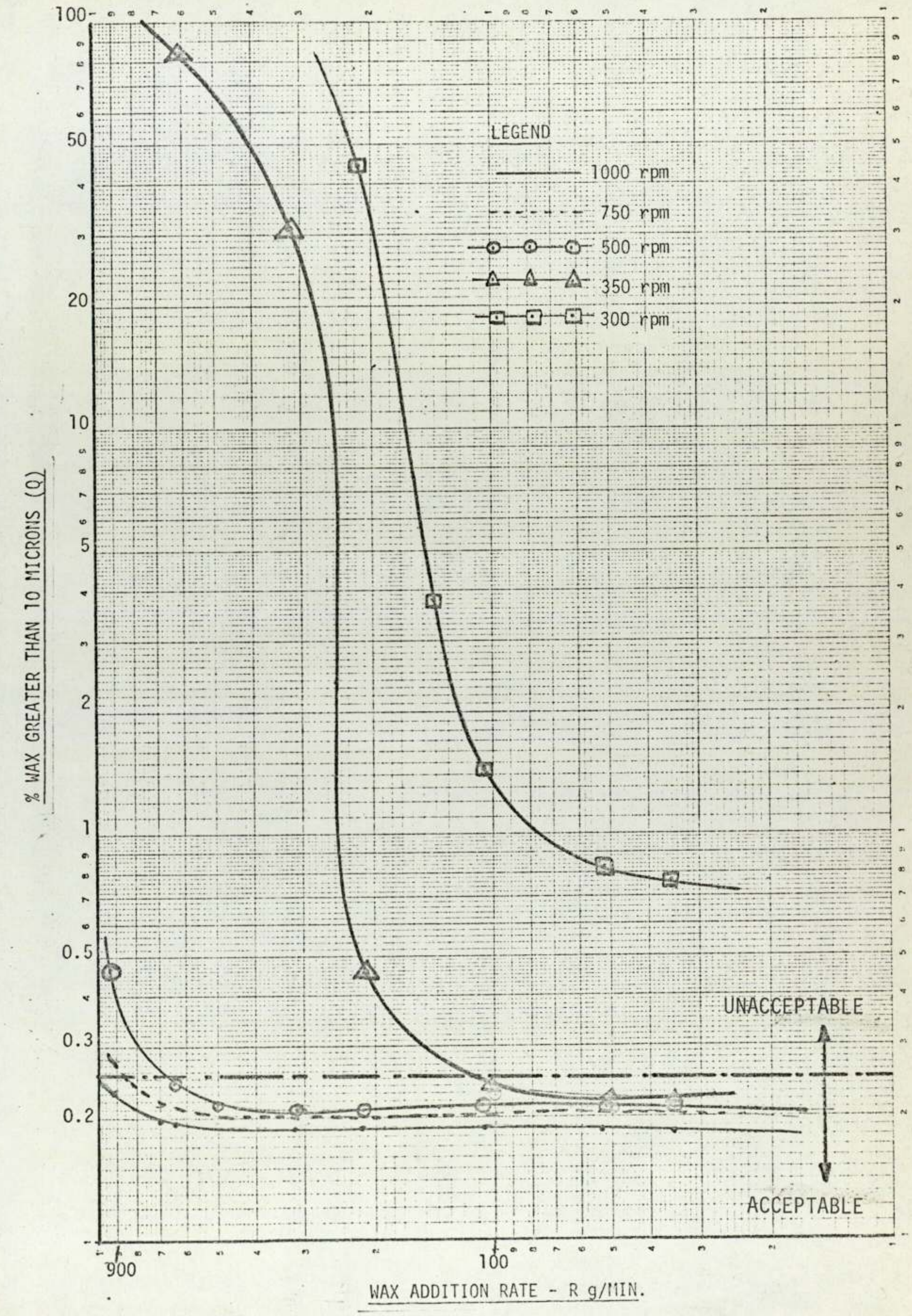
RESULTS

VARIABLE(S) STUDIED = COVARIATION OF AGITATOR SPEED
AND WAX FEED RATE

DATA SHEET NO R44

	BATCH NUMBERS						
Values of Other System Variables	241	242	243	244	245	246	247
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	125	132	123	126	130	123	126
Water T_w °C	94	95	94	94	93	95	93
Finished Emulsion T_e °C	Not measured	Not measured	93	92	91	92	91
Wax Processing							
Melting Time - mins	10.5	11	10	11	10	10	11
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	634	317	211	141	106	53	35
Cooling rate for emulsion °C/min	Not cooled	Not cooled	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	Complete	Complete	16.18	17.33	19.11	20.27	19.14
% Light Transmission	Overload	Overload	3	7	16	20	21
% Residue greater than 10mM	No quality	No quality	44.510	3.942	1.450	0.830	0.760
pH	parameters	parameters	9.6	9.7	9.8	9.9	9.9
Freeze/Thaw Cycles	measured	measured	Not measured	Not measured	> 10	> 10	> 10
Comments O/L = Overload	300 rpm. O/L	300 rpm. O/L	300 rpm. O/L	300 rpm. O/L	300 rpm. O/L	300 rpm. O/L	300 rpm. Slight O/L

FIGURE 5.7. - THE RELATION BETWEEN WAX ADDITION RATE AND PRODUCT QUALITY



Discussion.

The relationship between wax addition rate and agitator speed is well demonstrated in figures 5.6.and 5.7. and in data sheets R40, R41, R42, R43 and R44. On the laboratory apparatus, it was impossible to make a satisfactory wax emulsion below 350 rpm. irrespective of addition rate. However, the above results demonstrate that above the critical stirrer speed (See Section 5.6.), a well defined relationship exists between stirrer speed and wax addition rate. Each speed can handle a range of addition rates up to a maximum i.e. the "overload addition rate". As will be demonstrated in Section 5.6, the overload wax addition rate is a computable quantity, and experimental results may be correlated with theoretical values.

5.5.13. The Effect of Rate of Cooling of the Finished Wax Emulsion.

Experimental Techniques.

Because the literature had indicated that the above factor was a variable, several experiments were conducted to determine its importance. Wax emulsions made on the laboratory apparatus were normally cooled by pouring the batch into stoppered glass bottles and then submerging these in a laboratory sink filled with cold water. This technique reduced the temperatures of the emulsions from approximately 95°C to 20°C in about 10 minutes and proved to be very satisfactory and reproducible. This was defined as the standard rate of cooling.

With the other variables held at their standard settings, variations in cooling rates were tried from ambient (air) cooling to the refrigerated techniques already described in Section 4. The air cooling method meant that the freshly made emulsion would cool to ambient temperatures in about 3 hours. The refrigeration technique was achieved by transferring the freshly made emulsion into a metal beaker equipped with an agitator. The metal beaker was immersed in a second beaker containing fluorocarbon 12, the whole apparatus being contained in a fume cupboard. By allowing the fluorocarbon 12 to evaporate freely to atmosphere, (due to heat transfer from the emulsion), the wax emulsion was rapidly cooled to ambient temperature when the experiment was terminated.

Several batches of wax emulsion made under standard conditions were cooled at rates intermediate between ambient air cooling and refrigerated cooling and the results of all of these experiments are shown in data sheet R45.

VARIABLE(S) STUDIED = RATE OF COOLING FINISHED EMULSION

RESULTS

DATA SHEET NO R45

BATCH NUMBERS

Values of Other System Variables	247	248	249	250	251	252	253
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	131	125	130	120	128	125	126
Water T_w °C	93	95	94	96	94	93	95
Finished Emulsion T_e °C	94	96	95	96	95	94	97
Wax Processing							
Melting Time - mins	10	10	10	10	10	10	10
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	52.5	52.8	52	52.3	50.8	52.6	52.3
Cooling rate for emulsion °C/min	0.43	0.52	0.40	25.3	27	7	7
Quality Assessment							
Non Volatile Content of Emulsion	19.6	18.6	19.9	18.4	16.3	19.1	18.5
% Light Transmission	35	40	41	42	40	42	40
% Residue greater than 10mM	0.243	0.207	0.183	0.196	0.237	0.168	0.201
pH	9.9	9.9	10	10	10	10	10
Freeze/Thaw Cycles	>10	>10	>10	>10	>10	>10	>10
Comments	Ambient cooling Lab temp. 18°C.	Ambient cooling	Ambient cooling	Refrigerated	Refrigerated	STD cooling	STD cooling

Discussion.

Many wax emulsion processes stipulate rapid cooling following emulsification, presumably to minimise coalescence, or aggregation of wax particles. As data sheet R45 shows, the study emulsion is quite stable in this respect. In fact, there was little loss of translucency or increase in wax particulates greater than 10 microns. Nevertheless, this rule of thumb is generally speaking a good one, and previous experience with other emulsions (136) suggests that it may be mandatory with many formulae. The excess emulsifier used in the study emulsion (See Section 6) may give increased stability or, because the wax is so far below its drop point when emulsified, coalescence may be impossible and aggregation unlikely. Whatever the reasons are, even ambient cooling does not appear to significantly reduce the study emulsion quality.

5.5.14. The Effect of Water Hardness.

Technique.

The literature had reported that water hardness was a factor in controlling the emulsion quality. Previous experience suggested this was not so, due to the fact that many manufacturers use excess emulsifier in order to lower the wax melting point. Nevertheless, this was investigated by preparing artificially hardened samples of water for emulsification use. This was achieved by adding calcium carbonate and magnesium salts to create various degrees of hardness. These samples of water were subsequently converted into wax emulsions. The results of these experiments are shown in data sheet R46.

VARIABLE(S) STUDIED = WATER HARDNESS

RESULTS

DATA SHEET NO R46

BATCH NUMBERS

Values of Other System Variables	255	256	257	258	259	260	261
Emulsifiers							
Tergitol % w/w of formula weight	100	100	100	100	100	100	100
KOH % w/w of formula weight	100	100	100	100	100	100	100
Process Temperatures							
Wax Melt T_m °C	122	125	130	125	120	125	131
Water T_w °C	95	93	96	94	96	94	96
Finished Emulsion T_e °C	96	95	98	96	97	96	97
Wax Processing							
Melting Time - mins	10	10	10	10	10	10	10
Saponification Time - mins	5	5	5	5	5	5	5
Addition Rate g/min	53	53	53	53	53	53	53
Cooling rate for emulsion °C/min	7	7	7	7	7	7	7
Quality Assessment							
Non Volatile Content of Emulsion	19.9	18.3	20.3	19.1	18.7	19.6	18.4
% Light Transmission	38	40	41	35	29	15	5
% Residue greater than 10mM	0.191	0.227	0.184	0.254	0.194	0.222	0.270
pH	9.9	9.9	9.9	9.9	9.9	9.9	9.9
Freeze/Thaw Cycles	>10	>10	>10	8	9	6	2
Comments	200 ppm. (Standard)	400 ppm. Hardness	800 ppm. Hardness	1000 ppm. Hardness	1200 ppm.	1400 ppm.	1600 ppm.

The Effect of Water Hardness - Discussion.

A similar lack of effect is apparent with water quality. Many manufacturers of wax emulsions use soft water in order that the effect of the emulsifier is not impaired. Once again, the large excess of Tergitol used with the study emulsion seems to give extra protection. A reduction in emulsion quality, was only apparent after a hardness of some 8 times normal was simulated. When this occured both appearance and performance were affected. However, it may be concluded that, unless very hard water is used, there is no serious reason why quality should be affected. This is in agreement with the theory which states that nonionic emulsifiers should not be affected by hard waters.

5.6. The Relationship between Wax Feed Rate and Extent of Agitation.

5.6.1. Introduction.

In Section 5.5 a strong interdependence of the wax addition rate and the agitator speed was demonstrated. Graphs 5.6 and 5.7 showed the effect of overload on emulsion quality and from a manufacturers viewpoint, this situation should be avoided. Therefore it was of interest to investigate the submerging force required from the agitator in order that it would drag the wax stream below the water surface. It was further reasoned that if correlations were possible, then some important design rules could be formulated for surface type emulsification equipment.

The development of a force balance and subsequently a correlation between wax feed rate and downthrust force from the agitator is presented below for the laboratory equipment. Further data obtained on pilot and full scale manufacturing plant are also presented to confirm the validity of the correlation and to formulate practical design rules.

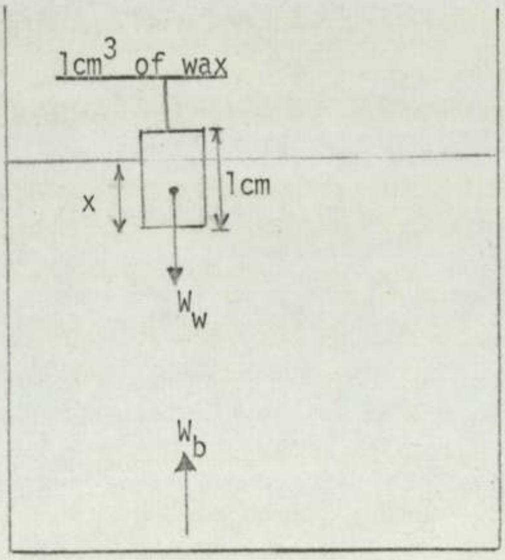
5.6.2. Data Sources.

The primary data used to derive the correlation between feed rate and downthrust requirement was that presented in Section 5.5.11/12. In addition, data was obtained by manufacturing the study emulsion in the pilot plant and the manufacturing facility at Johnson Wax. This is presented in Table 5.4.

5.6.3. Force Required to Submerge the Wax.

As already stated, the agitator is required to drag the wax below the water surface in order that it may emulsify prior to solidification. The force required to achieve this is dependent upon the wax feed rate, and a relationship may be developed from a consideration of the force on a 1cm cube of wax in a tank of water as shown in Figure 5.8. below:-

FIGURE 5.8. - SUBMERGING WAX BELOW WATER SURFACE



Let the density of the wax = ρ_o

Let the density of the water = ρ_w

TABLE 5.4. - EXPERIMENTAL WORK IN THE PILOT AND MANUFACTURING PLANTS.

PLANT USED	PILOT PLANT		MANUFACTURING PLANT	
Batch Size	200 Kg emulsion - 42.3 Kg wax melt		7452 Kg emulsion; 633.4 Kg wax melt	
Propeller Type	Marine 2/1 pitch		Marine 2/1 pitch	
Propeller Size	7.6 cm		38 cm	
Number of Propellers	1		2	
Speed of Rotation	1440 rpm		75	
Vessel Details	Unbaffled		Unbaffled	
Wax Temperature ^{o}C	125	130	128	121
Water Temperature ^{o}C	95	96	94	96
Addition Time - Minutes	$3\frac{1}{2}$	4	15.5	16
Addition Rate g/sec	201 g/sec	176 g/sec	681.1	659.8
Submerging Force required dynes/sec	18090	15855	61,298	59,382
Total force available dynes/sec	176,669	176,669	594,033	594,033
$\frac{\text{Total Force}}{10}$ dynes/sec	17,667	17,667	59,403	59,403
% Wax $>$ 10	0.236	0.194	0.241	0.217

As shown, most of the wax cube is below the water surface although a small part is above in the air.

By Archimedes Law, the weight of the wax cube W_w, is counter balanced by the buoyancy force exerted by the water W_b.

Also by the law of Archimedes, the weight of water displaced by the submergence of the wax = weight of wax = ρ_o (because it is a 1cm cube).

Therefore, the weight of water displaced = $X \times 1^2 \times \rho_w$

Where X is the part of wax cube below the surface.

Therefore
$$X\rho w = \rho_o$$
$$X = \frac{\rho_o}{\rho w}$$

Hence, if the wax is to totally submerge, a further volume of water must be displaced and the weight of this volume of water will be the minimum force required to submerge the wax.

Volume to be displaced $= 1^2 \times (1-X) = 1-\frac{\rho_o}{\rho w}$

Weight of displaced water $= \left(1-\frac{\rho_o}{\rho_w}\right)\rho_w = \rho_w - \rho_o$

Converting to force units, minimum force to submerge $1cm^3$ =

$$(\rho_w - \rho_o)g$$

Therefore, the minimum force (or down draft) to be produced by the agitator in order to submerge an incoming wax stream of R(g/sec) may be calculated by the expression:-

Minimum Force = $\dfrac{R(\rho_w - \rho_o)g}{\rho_o}$ since the weight of the cube $= \rho_o$

Substituting ρ_w = 1

ρ_o = 0.916 (137)

g = 980 cm/sec/sec

$$\text{Minimum Force} = \frac{R(1 - 0.916)980}{0.916}$$

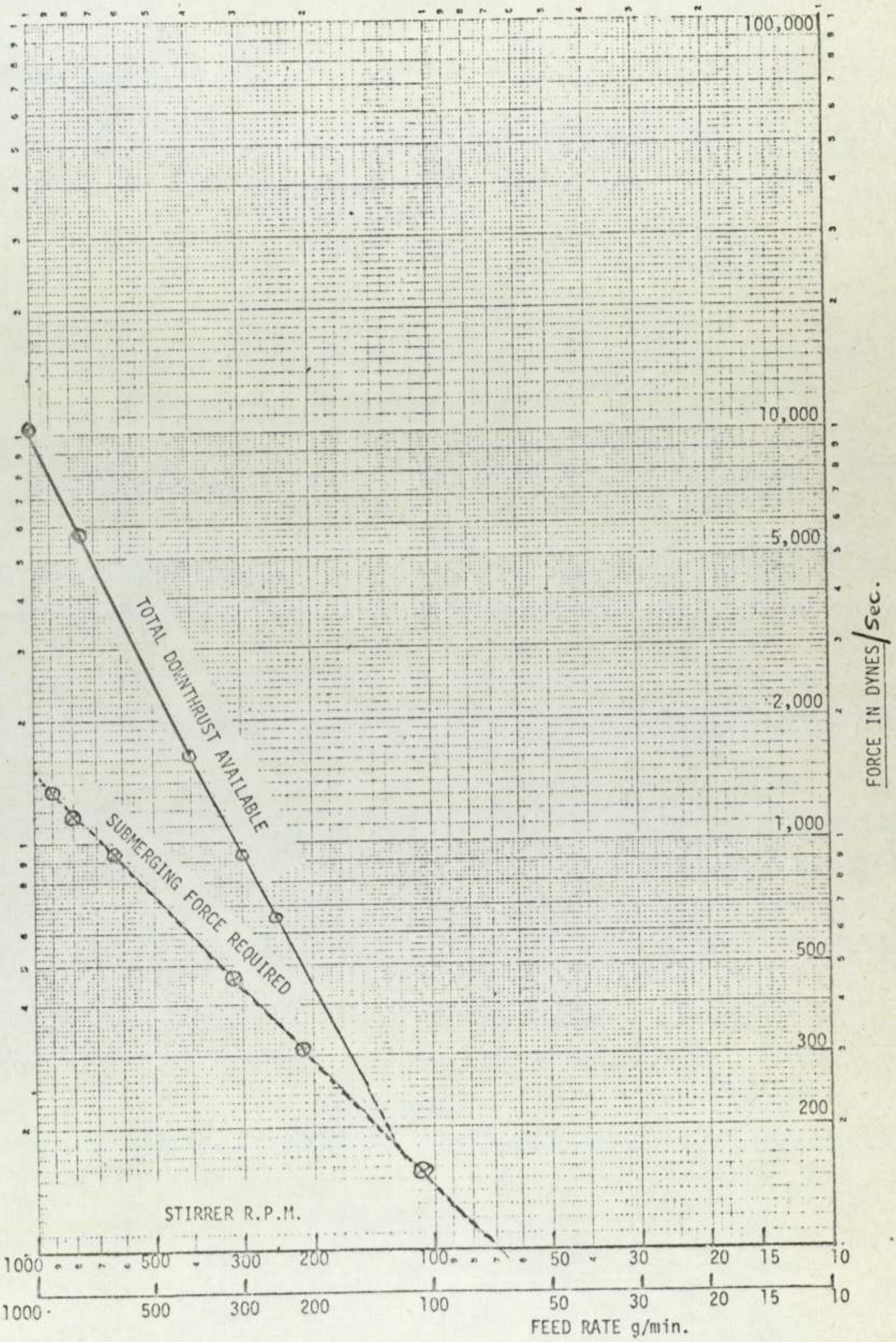
$$= \underline{90R \text{ dynes}}.$$

Using the equation for minimum submerging force developed above, the force requirement for various wax feed rates was calculated and this data is presented in Table 5.5. and in Figure 5.9. It was then of interest to compare this force requirement with the theoretical force developed by the agitator and this calculation is developed below:-

5.6.4. Calculation of the Total Force Developed by the Standard Laboratory Agitator.

The agitator utilised in the laboratory apparatus was a 3 blade marine propeller and the force produced at a particular speed may be calculated by a consideration of

FIGURE 5.9. - COMPARISON OF FORCE REQUIRED TO SUBMERGE WITH TOTAL DOWNTHRUST AVAILABLE.



the flows produced. According to the manufacturers data (138), a marine propeller produces axial flow and radial flow. Approximately 90 percent of the flow is axial and 10 percent radial. This axial flow is called 'primary flow', or 'pumping capacity' while the radial flow is termed 'head'. Rushton (139) showed that the 'primary flow' or 'pumping capacity' of a marine propeller (q) could be expressed by the relationship:-

$$q = KND_a^3$$

Where q = pumping capacity cm^3/sec.
n = number of propeller revolutions/sec.
Da = diameter of propeller - cm.
K = constant for the propeller depending primarily upon pitch and diameter.

Data obtained from one of the manufacturers of marine propellers (138) is plotted in Figure 5.10.

Taking readings for one set of values (since graph is straight line).

At 1 rev/sec. $n = 1$, $q = 4540$, $Da = 22.93$

$$q = 1 \times Da^3 \times K$$

$$\text{Therefore } \frac{q}{Da^3} = K = \frac{4540}{22.93} = \underline{0.378}$$

$$\text{Thus } q = nDa^3 \times 0.378$$

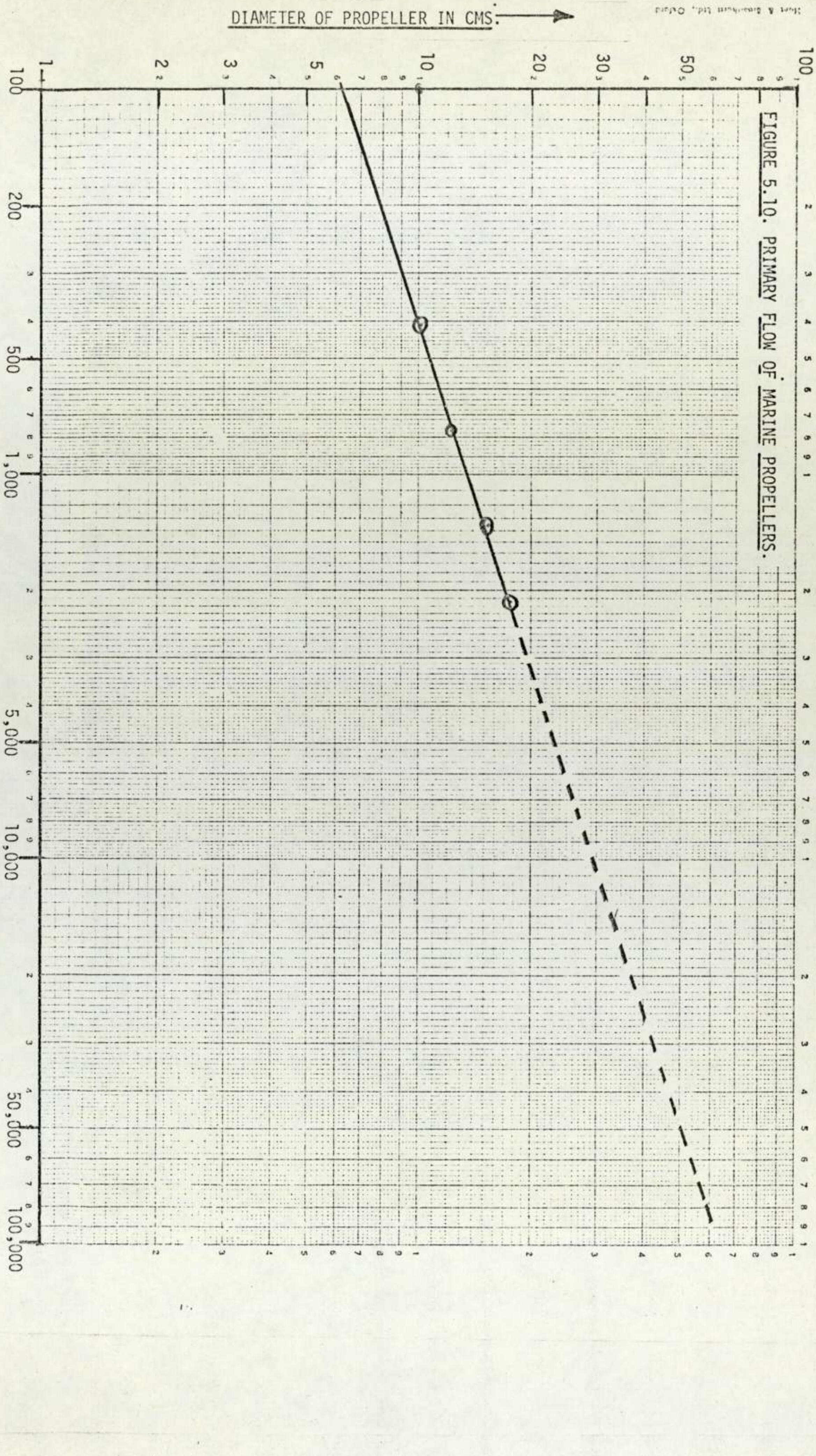


FIGURE 5.10. PRIMARY FLOW OF MARINE PROPELLERS.

Hence:-

q_{1000} = primary flow at 1000 rpm = $0.378 \times 4.5^3 \times 16.7$ = 575cm^3/sec

q_{750} = primary flow at 750 rpm = $0.378 \times 4.5^3 \times 12.5$ = 431cm^3/sec

q_{400} = primary flow at 400 rpm = $0.378 \times 4.5^3 \times 6.67$ = 230cm^3/sec

q_{300} = primary flow at 300 rpm = $0.378 \times 4.5^3 \times 5$ = 172cm^3/sec

q_{250} = primary flow at 250 rpm = $0.378 \times 4.5^3 \times 4.27$ = 144cm^3/sec

Figure 5.11 shows the typical flow pattern experienced in the laboratory emulsification vessel.

By calculating $\sum_{1}^{n} \delta f = F$ for the agitator at a specified speed, it is possible to compare the force required to submerge the wax stream with the total maximum downthrust forces generated by the propeller. This force will be at a maximum immediately downstream of the propeller and can be obtained as follows:-

<u>At 1000 rpm.</u>

Primary Volume flow = 575cm^3/sec = q

Projected Area Aa $= \dfrac{\pi Da^2}{4}$ = 15.9cm^2

Velocity $v = \dfrac{q}{Aa} = \dfrac{575}{15.9}$ = 36.7cm/sec

$$\frac{v^2}{2g} = \text{Velocity head (cm water)}$$

Therefore pressure developed downstream of propeller =

$$\frac{v^2}{2g} \times \text{density of water} = \frac{v^2}{2g}$$ (Assuming density of water is approx. 1)

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{F}{Aa} = \frac{v^2}{2g} \times g \text{ dynes/cm}^2$$

$$\text{Total force generated } F = \frac{v^2}{2} \times Aa = \frac{(q)^2 Aa}{(Aa)^2 \times 2} = \frac{q^2}{2A_a} \text{ dynes}$$

Substituting

$$F_{1000} = \frac{575^2}{2 \times 15.9} = \underline{10{,}397 \text{ dynes sec}^{-1}}$$

$$F_{750} = \frac{431^2}{2 \times 15.4} = \underline{5{,}842 \text{ dynes sec}^{-1}}$$

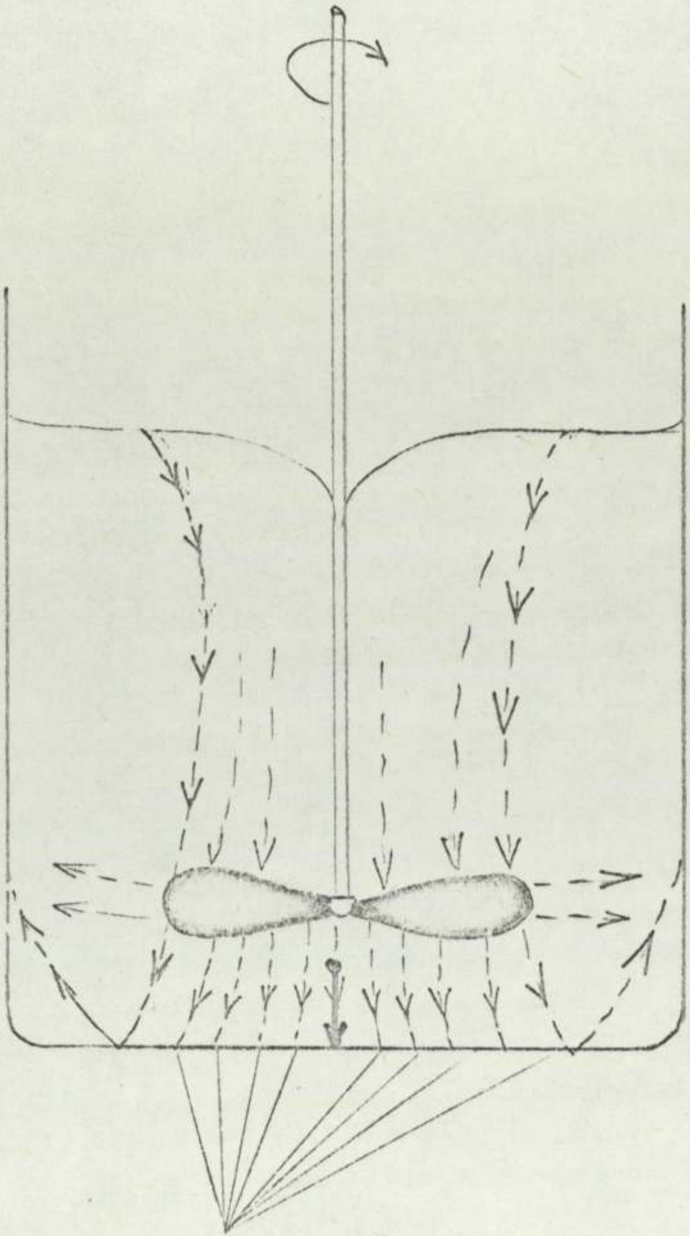
$$F_{400} = \frac{230^2}{2 \times 15.9} = \underline{1{,}664 \text{ dynes sec}^{-1}}$$

$$F_{300} = \frac{172^2}{2 \times 15.9} = \underline{930 \text{ dynes sec}^{-1}}$$

$$F_{250} = \frac{144^2}{2 \times 15.9} = \underline{652 \text{ dynes sec}^{-1}}$$

Similarly the total force generated was calculated for other speeds and is plotted against force requirements to submerge various wax feed rates. This data is summarised in Table 5.5. and plotted in Figure 5.9.

FIGURE 5.11. - FORCE PRODUCED BY PROPELLER



$\delta f_1, \delta f_2, \delta f_3 \text{------} \delta f_n$

TOTAL FORCE F. = $\sum_{i}^{n} \delta f$ ACTING OVER PROJECTED AREA Aa.

TABLE 5.5. - COMPARISON OF WAX SUBMERGING FORCE WITH AGITATOR GENERATED DOWNTHRUST

ADDITION TIME SECS	WAX ADDITION RATE (R)		MINIMUM SUBMERGING FORCE DYNES	AGITATOR SPEED(S) R.P.M.	TOTAL FORCE GENERATED DYNES	COMMENTS
	g/min	g/sec				
6.3	1000.0	16.7	1499	1000	10,400	Overload here.
10.0	534.3	10.6	951	1000	10,400	
30.0	211.4	3.5	317	1000	10,400	
60.0	105.7	1.8	159	1000	10,400	
120.0	52.8	0.9	79	1000	10,400	
6.3	1000.0	16.7	1499	750	5,800	Overload here.
10.0	634.3	10.6	951	750	5,800	Overload here.
30.0	211.4	3.5	317	750	5,800	
60.0	105.7	1.8	159	750	5,800	
120.0	52.8	0.9	79	750	5,800	
10.0	634.3	10.6	951	500	2,500	Overload here.
30.0	211.4	3.5	317	500	2,500	Overload here.
60.0	105.7	1.8	159	500	2,500	
120.0	52.8	0.9	79	500	2,500	
30.0	211.4	3.5	317	350	1,250	Overload here.
60.0	105.7	1.8	159	350	1,250	Overload here.
120.0	52.8	0.9	79	350	1,250	
30.0	211.4	3.5	317	300	930	Overload here.
60.0	105.7	1.8	159	300	930	Overload here.
120.0	52.8	0.9	79	300	930	Overload here.

5.6.5. Comparison of Required Submerging Force and Downthrust Generated by the Agitator in the Laboratory Apparatus.

From the overload data presented in Section 5.5. it was seen that overload occurred on the laboratory apparatus at various wax feed rates and agitator speeds. These are summarised in Table 5.5. and graphically in Figure 5.7. By inspection of Figure 5.7., when the overload condition is reached, the product quality (Q), deteriorates to a marked extent. However, if the wax addition rate is kept below the overload condition, in most cases, a satisfactory product results.

As stated earlier (See Section 5.5.8.), the purpose of the agitator is to provide downthrust to submerge the wax and induce shear forces to form droplets. It is likely that both conditions must be satisfied for the production of a satisfactory product, though it is probably that the submergence requirements are the overbearing ones.

A consideration of both the overload conditions and those immediately preceding them produced the following conclusions:-

(a). Wax feed rates just below the overload condition require approximately 10% of the total force produced by the agitator to effect submergence.

(b). When the submerging force required by the wax feed rate exceeds 10% of the total available force from the agitator, an overload condition is established resulting in substandard product (See Figure 5.9.).

(c). From (a) and (b) above, only 10% of the total force generated by the agitator is available as downthrust, i.e. to drag the wax below the water surface.

5.6.6. Comparison of required Submerging Force and Downthrust from the Agitator in Pilot and Full Scale Plant.

In order to confirm the conclusions from the laboratory studies detailed above, batches of the study emulsion were prepared on a 50 gallon and 600 gallon scale at Johnson Wax. Because of the cost in terms of plant time and raw materials, only two batches were made in each plant and the overload condition was not explored. The processing conditions used are summarised in Table 5.4. and are those normally used by Johnson when manufacturing this type of emulsion. These results further illustrate that only 10% of the force generated by agitator is available as downthrust.

5.6.7. Process Design Rules Embodying the Conclusions from Section 5.6.5.

(a). (i). With 'new' equipment, the designer should first decide upon:-

batch size.

wax addition rate coincident with reasonable batch time.

(ii). With existing plant, these variables are already fixed to a large extent.

(b). Having set batch size and addition rate as in (i) or (ii) above, the submerging force (in dynes) is calculated from:-

$$F_s = 90R$$

Where F_s = Minimum submerging force for a wax feed rate of R g/sec.

(c). Compute the total force available from the agitator(s) (F) as shown in 5.6.4.

(d). Compare F_s with $F_{\overline{TO}}$

If F_s is greater than $F_{\overline{TO}}$ an overload condition will exist therefore either increase the extent of agitation and repeat steps (a) to (d).

<u>OR</u>

decrease R then repeat steps (a) to (d).

If F_s is less than $F_{\overline{TO}}$, the design parameters are correct and the plant should prove satisfactory. However, it is probably advisable to make:-

F_s approximately $\frac{0.9F}{10}$ i.e. approximately $\underline{0.09F}$.

This should ensure that even surges in the wax feed rate may be dealt with.

Note that the above rules apply to systems agitated with marine propellers. They may be extended to other agitation systems providing that data on pumping capacity are available (See Section 5.6.4.).

5.7. Calculation of Minimum Emulsifier Level.

When contemplating the large scale manufacture of a wax emulsion it is important to know if one has a satisfactory formula. It is also possible that by following the equipment design rules detailed in the previous section that a reduction in emulsifier level might be attained. In either case, the value of the minimum emulsifier level for the emulsion of interest is a useful guide to stability and the possibility of obtaining a satisfactory product.

In Section 2.3., the literature dealing with the theory of emulsification was reviewed. The salient points were:-

The disperse phase of an emulsion consists of mostly spherical particles surrounded by emulsifier molecules.

The layer of emulsifier absorbed at the interface between oil and water i.e. surrounding the disperse phase particles, is usually monomolecular.

Using the above information coupled with certain assumptions, it is possible to calculate the minimum formula weight of emulsifier. This procedure is detailed below:-

5.7.1. Assumptions.

(a) That the disperse phase (wax) particles are spherical (b). That the mean particle diameter is known e.g. 1.0 microns.

(c). That the emulsifier molecules are positioned tightly over the outer (spherical) surface of the wax particle.

(d). That the formula weight of emulsifier is the sole agent governing particle size. Thus if a mean particle size of 0.5 micron is required, it is assumed that this is technically viable by the chosen emulsification method. It is recognised that this is not always correct.

5.7.2. Example of the Method.

It is required to emulsify a wax/solvent mixture with the formula shown below and the emulsifier is to be a nonionic fatty ester type with a molecular weight of 800.

Wax	=	1.064 % w/w
Oils	=	19.551 % w/w
Total oil phase	=	20.615

i.e. oil is approximately = 20.6 %.
water is approximately = 79.4 %.

Assume that it is required to produce 100g of emulsion and that the density of the oil phase is 0.8 g/cm^3.

Volume of oil phase $= \frac{20.615}{0.8} = 25.77\ \text{cm}^3$

Volume of 1 micron particle $= \frac{\pi D^3}{6} = \frac{3.14 \times 1^3}{6 \times 10^{12}} = \frac{0.524}{10^{12}}\ \text{cm}^3$

No. of particles to be produced $= \frac{\text{Volume of oil phase}}{\text{Volume of 1 particle}} = 49.18 \times 10^{12}$ particle

Surface Area of 1 micron particle $= \frac{\pi D^2 \text{cm}^2}{10^8} = \frac{\pi}{10^8}\ \text{cm}^2$

Total surface area to be covered by monomolecular layer of emulsifier molecules is given by surface area of one particle x No. of particles

$= 154.5 \times 10^4 \text{cm}^2$

Area of cross section of emulsifier molecules (1) $= 22\,^{o}\text{A}^{2}$

$= \frac{22}{10^{16}}\ \text{cm}^2$

Therefore assuming tight packing of molecules,

Number of molecules required $= \frac{154.5 \times 10^4 \times 10^{16}}{22}$

$= 7.023 \times 10^{20}$ molecules

Therefore, weight of emulsifier required

$= \frac{\text{Number of molecules}}{\text{Avogadro Number}} \times \text{molecular wt. of emulsifier} = 0.933$

5.7.3. Summary of the Method.

As illustrated by the above example, the method for estimating the formula weight of emulsifier may be broken down into a number of steps as follows:-

(a). Calculation of the total volume of oil or wax phase to be emulsified.

(b). Specification of the particle size required and from (a) above, calculation of the total number of particles to be produced.

(c). Calculation of the total surface area to be covered by emulsifier.

(d). By reference to Becher (1) or manufacturers data, the collection of information on the area of cross section of the emulsifier molecule and its molecular weight.

(e). Calculation of the weight of emulsifier used by the relation:-

$$\text{Weight of emulsifier} = \frac{A \times M}{a \times N}$$

Where A = Total surface area afforded by disperse phase.

M = Molecular weight of emulsifier.

a = Cross sectional area of emulsifier molecule.

N = Avogadro Number = 6.023×10^{23}

Results obtained with various Johnson emulsions are shown in Table 5. 6.

TABLE 5.6 . - CALCULATION OF FORMULA WEIGHT OF EMULSIFIER

FORMULA REFERENCE	DETAILS	ACTUAL % EMULSIFIER USED	CALCULATED MINIMUM % EMULSIFIER USED
JW 1	Multi surface aerosol polish incorporating low melting point waxes and solvents.	1.21	0.933
JW 2	Buffable floor polish emulsion.	2.12	1.030
JW 3	Aerosol furniture polish emulsion incorporating solvents and low melting point waxes.	1.12	0.990
JW 4	Emulsion for Auto polish incorporating low melting point waxes.	2.29	2.180
Study emulsion	Based on intermediate for Drybright floor polish.	3.10	0.600

5.7.4. Conclusions.

A study of the formulations within Johnson (136), those published by Allied Chemicals (76) ; Petrolite Waxes (79), and Hoechst Waxes (77) indicated that the emulsifier concentration can be between 0.5 and 10% w/w of the formula. In general, the calculation method outlined above produces a minimum level of emulsifier which is usually exceeded in practice. Formulae incorporating low to medium melting point waxes and for solvents are usually readily specified by the above procedure. However, formulae containing higher melting waxes such as the polyethylenes usually require higher amounts of emulsifier than predicted by the above method. This is believed to be for the following reasons:-

(a). To reduce the wax drop point in order that atmospheric surface emulsification may be used.

(b). To take account of the phase change which occurs and to delay or reduce its effects e.g. the increase in interfacial tension.

(c). To provide ample emulsifier to stabilise the smaller particles.

In such cases it is common to use 2 - 5 times the minimum level of emulsifier.

5.8. Analysis of the Relationship between the Major Variables.

5.8.1. Introduction.

During the literature review dealing with 'System Variables', presented in Section 2.2., it was found that Lange et al., (81) had used mathematical/statistical methods to produce a relationship between the system variables and a parameter of quality namely "Dry-bright effect". This latter quantity was a measured value relating to the amount of gloss produced by applying various floor polish products to a specified substrate. Using a similar approach, it was decided to attempt to describe the general relationship between the variables governing emulsion quality when using the atmospheric surface addition method.

5.8.2. Selection of Key Variables.

It was concluded in Section 4 that wax emulsion quality may be classified into two categories, namely appearance and performance. It was further concluded that appearance is best quantified by gravimetrically assessing the quantity of wax greater than 10 microns and that performance can be conveniently measured by freeze thaw testing. Therefore it should be possible to relate the system variables to a quality parameter (Q) which may be either percentage of wax greater than 10 microns or the number of freeze thaw cycles completed.

A review of the majority of the results presented in

Section 5 confirmed that the study emulsion was very stable. Only considerable reductions in emulsifier level and/or high alkalinity seemed to significantly reduce its performance parameter. However, major changes in appearance, which may effect performance characteristics (example lumps or creaming) were readily caused by changes in several of the system variables. Therefore the appearance parameter was selected as the criterion of quality and it was decided to investigate the relationship between Q (percent wax greater than 10 microns) and the other system variables.

Having defined Quality Q as the percent greater than 10 microns in diameter the other system variables were defined as follows:-

Emulsifier Level : E as percentage of formula weight.
Alkali Level : A as percentage of formula weight.
Stirrer Speed : S as revolutions per minute.
Wax Addition Rate : R as gms/minute.

All other identified variables (See Table 5.1.) were excluded from this analysis on the grounds that they have been found to be relatively insignificant and can be readily specified at optimum and practical values as follows:-

Wax Temperature : 10 - 15^{o}C greater than wax drop point (i.e.108 - 113^{o}C).

Water Temperature : 95^{o}C i.e. maximum controllable temperature at 1 atmosphere.

Saponification Time : 5 minutes - based on experiments in Section 5. .

Extent of Wax Agitation. : Sufficient to give complete saponification in 5 minutes.

Rate of Cooling : 7^{o}C/minute.

Water Hardness : 500ppm maximum.

A suitable regression package was then selected from the Honeywell time sharing library. This programme was called SMLRP (stepwise multiple linear regression programme) and is presented in appendix II. The way in which this was used is described in the next section.

5.8.3. Use of the SMLRP Programme.

There were two multiple linear regression programmes in the Honeywell library but only one of these would accept all of the available data, namely 132 data points and the ready use of transforms. which are explained later and in Appendix II.

The initial run was made with a data file built up of the raw data i.e. no transforms. The results of this run are summarised in Table 5.8. From these results it was concluded that transforms would be required and reference was made to the graphs of E, A, S and R versus the dependent variable Q in Figures 5.1.; 5.2.; 5.6. and 5.7.in order to determine which transforms might be required.

Q versus E (Figure 5.1.).

This curve was judged to be parabolic and the following transforms were attempted:-

Log Q
E
E^2
Log E
$(\text{Log } E)^2$

Q versus A (Figure 5.2.). This curve was also judged to be parabolic and the same transforms as for E were used.

Q versus S (Figure 5.6.). This curve appeared to be approximately hyperbolic and the following transformations were listed for trial:-

Log Q
S
S^2
$\frac{1}{S}$
$\frac{1}{S^2}$

Q versus R (Figure 5.7.).

This was considered to be the most difficult data on file. The cubic appearance suggested the following transforms.

Log Q

R

R^2

R^3

Log R

$(\text{Log } R)^2$

$(\text{log } R)^3$

Interaction Terms.

From the experimental work it was found that at least two of the key variables were interdependent namely R and S. It was also considered likely that other interaction terms would be necessary in order to obtain a good fit. These terms were devised by the use of a matrix as shown in Table 5.7. below. In this matrix T_1, T_2, T_3 ----- T_n are the transforms already discussed above. Blanks in the matrix indicate either repeated interaction terms of where the product of transforms equal unity.

TABLE 5.7. MATRIX FOR TRANSFORM INTERACTIONS

TRANSFORMS	T_1	T_2	T_3	T_4	$\frac{1}{T_1}$	$\frac{1}{T_2}$	$\frac{1}{T_3}$	$\frac{1}{T_4}$
T_1	T_1^2	T_1T_2	T_1T_3	T_1T_4	-	$\frac{T_1}{T_2}$	$\frac{T_1}{T_3}$	$\frac{T_1}{T_4}$
T_2	-	T_2^2	T_2	T_2T_4	$\frac{T_2}{T_1}$	-	$\frac{T_2}{T_3}$	$\frac{T_2}{T_4}$
T_3	-	-	T_3^2	T_3T_4	$\frac{T_3}{T_1}$	$\frac{T_3}{T_2}$	-	$\frac{T_3}{T_4}$
T_4	-	-	-	T_4^2	$\frac{T_4}{T_1}$	$\frac{T_4}{T_2}$	$\frac{T_4}{T_3}$	-
$\frac{1}{T_1}$	-	-	-	-	$\frac{1}{T_1^2}$	$\frac{1}{T_1T_2}$	$\frac{1}{T_1T_3}$	$\frac{1}{T_1T_4}$
$\frac{1}{T_2}$	-	-	-	-	-	$\frac{1}{T_2^2}$	$\frac{1}{T_2T_3}$	$\frac{1}{T_2T_4}$
$\frac{1}{T_3}$	-	-	-	-	-	-	$\frac{1}{T_3^2}$	$\frac{1}{T_3T_4}$
$\frac{1}{T_4}$	-	-	-	-	-	-	-	$\frac{1}{T_4^2}$

Use of the transforms.

The regression programme allowed some 20 transformed variables to be used per run. Initially the transforms listed above were run and a 75.11% fit was obtained. Next followed a series of runs where various interaction transforms were incorporated and the overall results inspected for goodness of fit and the significance of individual transformed variables. This was achieved as follows:-

(a). Goodness of fit was measured by the final value of R^2 (Printed by the computer as R-sq). R is the correlation coefficient and R^2 may be taken as the fraction of the variation of the independant variable (or transformed variable) accounted for by any given equation.

(b). A measure of the dependence of Q on any particular transformed variable (transform), was given by an F-ratio associated with that transform in the final regression equation. The greater the F-ratio, the greater the confidence level with which the significance of that transform may be assumed.

A summary of the best set of results is shown in Table 5.9. (a) and the resultant equation is detailed below.

$$\text{Log } Q =$$

$$- 11.21 - 0.004\ S + 0.009\left(\frac{S}{E}\right)^2 - 10.58\ \frac{R}{S} + 3313.7\ \frac{R}{S^2}$$

$$+ 6.65\ \frac{(\text{Log } S)}{(\text{Log } R)^2} + 3 \times 10^{-20}\ EA^2 - 4.35\ \frac{E}{S} - 5.3 \times 10^{-5}\ EA - 0.77(\text{Log } A)^3$$

$$+ 0.29\ (\text{Log } E)^3 + 3 \times 10^{-6}\ R^2 + 3.28\ (\text{Log } A)\ (\text{Log } R)$$

By inspection the above equation is somewhat cumbersome even though it accounts for an overall fit of 95.15%. By reference to the data presented in Table 5.9.(b), it was deduced that seven terms accounted for 91.12% of the values of the dependant variable Q. Therefore the programme was re-run using only seven terms which are listed below:-

$$\left(\frac{S}{E}\right)^2;\quad \frac{R}{S};\quad \frac{R}{S^2};\quad \frac{(\text{Log } S)}{(\text{Log } R)^2};\quad \frac{(\text{Log } R)}{(\text{Log } S)};\quad \frac{EA^2}{10^{14}};\quad (\text{Log } A)^3$$

A summary of the results is presented in Table 5.9. (b) and the equation below:-

$$\text{Log } Q =$$

$$- 10.22 + 0.007\left(\frac{S}{E}\right)^2 - 4.15\ \frac{R}{S} + 1453.6\ \frac{R}{S^2}$$

$$+ 4.41\ \frac{(\text{Log } S)}{(\text{Log } R)^2} + 11.9\ \frac{(\text{Log } R)}{(\text{Log } S)} + \frac{2EA^2}{10^{20}} - 0.35\ (\text{Log } A)^3$$

Further inspection indicated that the sixth term namely $\frac{2EA^2}{10^{20}}$ would always be very small and accordingly a further reduction was made by excluding it. The final run was then made and the

TABLE 5.8.
RESULTS OF THE S.M.L.R.T. RUNS

OBSERVED VALUE OF Q	CALCULATED VALUE OF Q VIA RAW DATA	CALCULATED VALUE OF Q WITH 95% FIT	CALCULATED VALUE OF Q WITH 90% FIT
0.5050	23.4365	0.4419	0.9685
0.3490	21.8576	0.2880	0.4164
0.2470	20.2736	0.2523	0.2520
0.2010	18.6997	0.2466	0.1642
0.2150	15.5417	0.2550	0.1336
0.2180	12.3838	0.2595	0.1211
0.2020	7.6470	0.2460	0.1308
0.1930	2.9101	0.2160	0.1673
0.2100	-0.2478	0.1977	0.2115
0.1900	-16.0374	0.1331	1.3038
1.1500	-3.5508	0.6073	1.1550
0.3050	-1.9028	0.3496	0.4199
0.2910	-1.9028	0.3496	0.4199
0.2100	-1.5732	0.3118	0.3590
0.2300	-0.9140	0.2507	0.2730
0.2050	-0.2548	0.2058	0.2178
0.1350	0.4044	0.1733	0.1818
0.1650	1.3932	0.1416	0.1498
0.1590	1.3932	0.1416	0.1498
0.1480	3.0411	0.1189	0.1310
0.1410	4.6891	0.1234	0.1420
0.1490	6.3371	0.1593	0.1876
0.1800	7.9850	0.2558	0.2987
0.2500	9.6330	0.5104	0.5676
5.1000	12.9290	3.8744	3.4024
3.1050	12.9290	3.8744	3.4024
0.1900	-0.5540	0.1450	0.1178
0.1850	0.1052	0.1249	0.1043
0.1550	1.0939	0.1072	0.0950
0.1350	2.7419	0.1017	0.1009
0.1250	2.7419	0.1017	0.1009
0.1260	4.3899	0.1254	0.1376
0.1350	6.0378	0.2020	0.2371
0.2600	9.3338	1.1719	1.3557
0.2090	-1.2132	0.1740	0.1399
0.2250	-2.2020	0.2409	0.2006
0.2100	-2.2020	0.2409	0.2006
0.2500	-3.8500	0.4305	0.5051
0.2000	-0.2548	0.2058	0.2178
0.2500	-0.1950	0.2700	0.2995
0.3900	-0.1052	0.5762	0.6554
1.2500	-0.0454	1.4745	1.5697
0.1990	-0.2543	0.2058	0.2178
0.2010	-0.2548	0.2058	0.2173
0.2050	-0.3147	0.1743	0.1746
0.1850	-0.4044	0.1530	0.1408
0.1690	-0.5540	0.1450	0.1178
0.1550	-0.8533	0.1581	0.1114
0.1500	-0.9729	0.1654	0.1146
0.1470	-0.9729	0.1654	0.1146
0.1430	-1.0328	0.1689	0.1159
0.1440	-1.1525	0.1748	0.1227
0.1450	-1.4517	0.1822	0.1426
0.1600	-1.7509	0.1771	0.1693
0.1300	-2.0502	0.1614	0.2029
0.1900	-2.0502	0.1614	0.2029
0.1590	2.9813	0.1051	0.1130
0.1430	2.8915	0.0980	0.1015
0.1300	2.7419	0.1017	0.1009

TABLE 5.8.
RESULTS OF THE S.M.L.T.R.T. RUNS

```
 OBSERVED        CALCULATED        CALCULATED       CALCULATED
  VALUE          VALUE OF Q        VALUE OF Q       VALUE OF Q
   OF Q        VIA RAW DATA       WITH 95% FIT     WITH 90% FIT
  0.1350          2.4427            0.1239           0.1317
  0.1580          2.1435            0.1609           0.1962
  0.1950          1.8442            0.1651           0.3038
  0.1890          3.1010            0.1439           0.1669
  0.2250          3.1907            0.2948           0.3244
  0.3100          3.2506            0.7138           0.7247
  2.0100         -0.0154            2.9645           2.9553
  0.4150         -0.1052            0.5762           0.6554
  0.2650         -0.1950            0.2700           0.2995
  0.2150         -0.2548            0.2058           0.2178
  0.2000         -0.3147            0.1743           0.1746
  0.1900         -0.3745            0.1579           0.1494
  0.1710         -0.5540            0.1450           0.1178
  0.1630         -0.7036            0.1495           0.1111
  0.1550         -0.8533            0.1581           0.1114
  0.1440         -1.1525            0.1748           0.1227
  0.1450         -1.4517            0.1822           0.1426
  0.1600         -1.7509            0.1771           0.1693
  0.1810         -2.0502            0.1614           0.2029
  0.7500         21.6970            0.6350           0.5153
  0.8800         21.9065            0.3135           0.4733
  1.0300         22.1858            0.8333           1.2845
  1.6500         22.3953            2.1537           2.7452
  0.2140         20.3275            0.2493           0.2830
  0.2450         20.7465            0.6076           0.7630
  0.3300         21.1655            1.6793           2.0717
  4.6000         21.5845            4.0095           4.7302
  0.2000         15.8700            0.2096           0.1571
  0.2050         16.5683            0.3276           0.3517
  0.2080         17.2666            0.3902           0.5816
  0.2100         17.9649            0.3906           0.7658
  0.2150         18.6632            0.3675           0.8667
  0.2300         19.3616            0.3473           0.8624
  0.2550         20.0599            0.3436           0.8310
  0.3200         20.7582            0.3654           0.7372
  0.4700         21.4565            0.4257           0.6240
  0.2000          7.9752            0.1549           0.1056
  0.2000          8.6735            0.1912           0.1580
  0.2000          9.3718            0.1976           0.2012
  0.2000         10.0701            0.1767           0.2145
  0.2000         10.7685            0.1504           0.2018
  0.2050         11.4668            0.1296           0.1734
  0.2120         12.1651            0.1174           0.1394
  0.2300         12.8634            0.1147           0.1064
  0.2800         13.5617            0.1230           0.0779
  0.1900          0.0804            0.1169           0.1410
  0.1900          0.7787            0.1597           0.1837
  0.1900          1.4770            0.1955           0.2238
  0.1900          2.1753            0.2112           0.2361
  0.1920          2.8737            0.2194           0.2236
  0.1950          3.5720            0.2317           0.1956
  0.1950          4.2703            0.2581           0.1611
  0.2000          4.9686            0.3108           0.1266
  0.2250          5.6670            0.4115           0.0958
 40.0500         26.5944           69.0626         127.4532
 43.5010         12.6297           19.6747          17.6930
 30.0500         12.6297           19.6747          17.6930
 25.1200          0.0444           26.7181          20.0602
 21.4500          0.0444           26.7181          20.0602
 40.5000          3.3404           11.7967           8.0293
 25.5000          0.0444           26.7181          20.0602
  9.0000         22.6048            5.0930           5.5569
 34.0000         22.8841           15.0079          13.0910
 48.0000         23.0238           25.0970          19.4787
 61.0000         23.1634           41.3490          28.4706
 74.0000         23.3031           67.2505          40.9545
 98.0000         23.5824          172.3303          81.3017
 24.5000         22.0035            8.5723           9.4609
 41.0000         22.4225           17.0909          17.1585
 57.0000         22.8415           32.7301          28.8947
 71.0000         23.2604           61.4804          45.9231
 84.0000         23.6794          114.9949          69.6851
 98.0000         24.0984          216.5707         101.8148
ENTER A 1,2,3 OR 4FOR:  1-SELECT NEW DATA FILE
2-SELECT NEW VARIABLES, 3-SELECT NEW 'F' OR 'CL',
4-END OF RUN
=
```

TABLE 5.9 - SUMMARY OF MULTIPLE REGRESSION RUNS.

RUN	TRANSFORMED VARIABLE	F-RATIO	VALUE R^2 IN FINAL EQUATION	COEFFICIENT
(a)	S	117	0.9515	0.004
	$(S/E)^2$	322	0.9515	0.009
	R/S	205	0.9515	-10.58
	R/S^2	311	0.9515	3313.7
	$(\text{Log } S)/(\text{Log } R)^2$	46	0.9515	6.7
	$EA^2 \times 10^{-14}$	231	0.9515	3×10^{-20}
	E/S	26.8	0.9515	-4.35
	EA	11.7	0.9515	-5.3×10^{-5}
	$(\text{Log } A)^3$	133.5	0.9515	-0.77
	$(\text{Log } E)^3$	28	0.9515	0.29
	R^2	53	0.9515	3×10^{-6}
	$(\text{Log } A)\ (\text{Log } R)$	73	0.9515	3.28
(b)	$(S/E)^2$	407	0.9112	0.007
	R/S	236	0.9112	-4.15
	R/S^2	413	0.9112	1453.6
	$(\text{Log } S)/(\text{Log } R)^2$	17	0.9112	4.41
	$(\text{Log } R)/(\text{Log } S)$	28	0.9112	11.9
	$EA^2 \times 10^{-14}$	175	0.9112	2×10^{-20}
	$(\text{Log } A)^3$	93	0.9112	-0.35
(c)	$(S/E)^2$	107	0.7859	0.005
	R/S	76	0.7859	-3.59
	R/S^2	161	0.7859	1400.4
	$(\text{Log } S)/(\text{Log } R)^2$	4.3	0.7859	3.38
	$(\text{Log } R)/(\text{Log } S)$	6.5	0.7859	8.76
	$(\text{Log } A)^3$	22	0.7859	-10.18

results are presented in Table 5. 9. (c) and the equation below.

$$\text{Log } Q =$$

$$- 10.176 + 0.005 \left(\frac{S}{E}\right)^2 - 3.592 \frac{R}{S} + 1400.36 \frac{R}{S^2}$$

$$+ 3.381 \frac{(\text{Log } S)}{(\text{Log } R)^2} + 8.76 \frac{(\text{Log } R)}{(\text{Log } S)} + 0.096 (\text{Log } A)^3$$

Conclusions.

The quality of the study emulsion may be judged by the percentage of wax particles greater than 10 microns (See Section 4.4.4.).Denoting this quality as Q, it can be shown to be a dependant variable to the other key variables of the system (E; A; R; S.) by an empirical equation with seven terms. This equation has been shown to account for 91% of the values of Q.

Further improvements to the above relationship are possible but it is likely that larger equations will be required and/or consideration of the effects of the minor variables.

The significance of the key variables as they relate to the value of Q may be summarised as follows:-

$$S > A > R > E$$

5.9. Conclusions on System Variables.

(a). The emulsification of wax can only occur if the wax is in the liquid phase.

(b). During emulsification, a finite amount of work must be performed on the wax to form droplets, and therefore a finite amount of time is required to effect emulsification. Though this emulsification time is small, the wax must be molten throughout and this in turn means that the temperature difference between wax and water is critical. It is concluded that the temperature difference between the water and the wax drop point is the critical parameter and that this value must not exceed 15°C.

(c). When the above conditions are adhered to, a gradation of the wax emulsification system variables is then possible. These are shown below in decreasing order of importance:-

$$S > A > R > E$$

This is however based on a mathematical model, which accounts for the variations of these key variables to a limited extent. (See Section 5.8.)

(d). By a consideration of the downthrust requirements associated with a particular wax feed rate, the appropriate agitation system may be designed and/or provided.

(e). Only approximately 10 percent of the force generated by the agitator is available to submerge the wax. Therefore, if the wax can be introduced below the surface in a satisfactory manner, it is possible that a reduction in power may be possible.

(f). Variations in wax emulsion quality may be effected by altering the level of emulsifier(s). However, the practical limits for such alterations are from 75 to 230 percent of the formula weight in the case of the study emulsion.

(g). Similar variations in wax emulsion translucency may be obtained by the variation of the level of alkali but with levels that are increased much beyond the formula weight, decreased product stability is a consequence. Practical limits for the study emulsion are from 75 to 125 percent of the formula weight.

(h). Provided the temperature difference considerations detailed in 5.9.1. above are complied with, product quality Q, measured in terms of percent wax greater than 10 microns, may be predicted by the general equation:-

$$\text{Log } Q =$$

$$-10.176 + 0.005\left(\frac{S}{E}\right)^2 - 3.592\frac{R}{S} + 1400.36\frac{R}{S^2}$$

$$+ 3.381\frac{(\text{Log } S)}{(\text{Log } R)^2} + 8.76\frac{(\text{Log } R)}{(\text{Log } S)} + 0.096(\text{Log } A)^3$$

6. INVESTIGATION INTO THE MECHANISM OF WAX EMULSIFICATION

6.1. Introduction

So far, the study has dealt with the assessment of wax emulsion quality and the variables controlling it. Therefore the final major objective is to investigate, and try to understand the mechanism by which a molten stream of wax is converted into an emulsion. Although this may not appear to be of large interest to industry, it is highly probable that if the mechanism were better understood, improvements to processing equipment and ultimately to product quality would follow. This section will examine the process of combining wax and water phases by the technique of surface addition, to form a stable satisfactory emulsion.

6.2. Main Conclusions from the Literature Survey

These conclusions fall into two main categories as follows:-

6.2.1. Those dealing with theoretical explanations on liquid-liquid emulsion structure and stability.

6.2.2. Those dealing with the mechanics of disruption processes and ways of effecting droplet or particulate formation from the disperse phase.

These will now be discussed in greater detail.

6.2.1. Conclusions Regarding the Structure of Wax Emulsions.

(a). There is almost no information to be gained from the literature regarding theory or structure of wax emulsions.

(b). There are few publications specifically mentioning wax emulsions, and it appears to be generally assumed that these emulsions have the same basic structure as conventional liquid/liquid products. The situation is quite different with liquid/liquid emulsions, where the literature is extensive. The main conclusions are discussed briefly below.

(i). The theories concerned with the identification of emulsifying agents as mainly surface active materials by Quincke (140), and Donnan and Potts (141) were perhaps the first to have established importance of the emulsifier in lowering the interfacial tensions.

(ii). The existence of some emulsifying materials which were not surface active e.g. gums and fine solids, caused more work to be done by Bankroft (93) who pointed out the significance of the Gibbs equation regarding thermodynamic stability.

(iii). Perhaps the biggest breakthrough resulted from the work of Harkins (101) and others (95), resulting in the so-called orientated wedge theory. This theory explained the stability of emulsions by virtue of the fact that all emulsifiers were seen to have an oil soluble group at one end of the molecule and a water soluble one at the opposite end. The theory postulated that during the process of emulsification, the emulsifier molecules orientated themselves around the disperse phase, so as to surround each droplet with a unimolecular layer of emulsifier. Droplet coalescence was seen to be prevented by the fact that the emulsifier molecule 'ends' presented to the exterior were those soluble in the continuous phase. For example, an oil in water emulsion would have the (disperse phase) oil particles coated on the exterior with water soluble ends of the molecule making particle coalescence unlikely. Though the theory has been developed and refined since the time of Harkins, it still presents the main explanation for most events in emulsion technology.

(iv). More recent theories explain the structure of the emulsions on the basis of electrical forces at the interface. The work of Van Den Tempel (142) and of Overbeek (143) are typical of the trends towards a consideration of electrical double layers at the interface. Perhaps one of the main reasons why there is great interest in this area is the fact that major improvements in instrumentation have been effected, making many of the theoretical considerations verifiable by electrical measurements.

6.2.2. Conclusions on Droplet Production.

The actual process of disruption of a continuous oil phase into discrete droplets or particles, is seen to be one of supplying energy to overcome surface tension forces.

The literature cites some examples of mechanisms by which droplets may form. These may be summarised as follows:-

(a). The disruption of a plane interface by the act of simple shaking or agitating, thereby inducing lamellae or "fingers" of one phase penetrating into the other phase. The work of Gopal is typical of the thinking in this area (24)

(b). The disintegration of liquid jets into droplets by sinusoidal modulations and varicose deformations. The classical work of Richardson (85) gives photographic evidence of these mechanisms.

(c). The use of ultrasonics to effect droplet formation which was first described by Polhman (144). A summary of the developments and theory is presented by Sherman (24), who records the mechanism as a series of compressions and rarefactions within the emulsion. Minute gas bubbles attain pressures of several hundred atmospheres during the compression phases, eventually collapsing to form droplets.

(d). The use of high voltage emission to produce monodisperse emulsions has been known since the 1950's (145). The method is something of a scientific curiosity, and has received little attention from a commercial viewpoint. The mechanism is not fully understood but is thought to be due to charged emulsion particles being streamed away from a point source.

By examination of the droplet formation processes, it was seen that (c) and (d) above did not apply to the system under study (surface addition of wax to water). However, processes (a) and (b) both presented possibilities in explaining a droplet production mechanism.

6.2.3. Plan of Experimental Work.

In view of the doubt surrounding the actual mechanism of emulsification, it was decided to film the process using high speed photography. It was hoped that high speed photographs would show what occurred on a macro scale. However, it was also decided that photomicrography would be necessary to further illustrate the process in view of the size range of emulsified wax particles. With this in mind, an apparatus was constructed to be used in conjunction with the microscope in order to view the emulsion making process and photograph each stage.

6.3. Description of Apparatus.

6.3.1. Apparatus for Visual Experiments.

The apparatus described in Section 5 for the investigation of variables was used for the initial visual experiments with the exception of the isomantle normally used to heat the emulsion water. This was replaced by an electric hot plate in order to give an unrestricted view of the water phase. The same apparatus was used for the high speed still photographs and the arrangement of camera and lighting is shown in

Figure 6.1.

6.3.2. High Speed Cine Photography.

Once again, the standard emulsification apparatus was used together with a Hitachi H16 high speed cine camera. Illumination was by a photoflood lamp mounted above and behind the emulsification vessel. The arrangement for photography is shown in Figure 6.2.

On completion, the films were reviewed through an editing projector and frames selected for the production of still photographs in 7½ cm x 9cm format. These stills were produced using a Vickers M17 optical microscope as shown in Figure 6.3. The diagram shows the film held in position over the microscope light source by means of hinged coverslips. By using the low power objective and focusing the microscope condenser, it was possible to take a photomicrograph of the desired frame.

6.3.3. Apparatus for Spontaneous Emulsification.

Filaments for these experiments (See Section 6.4.4.) were produced on the normal wax emulsification equipment. These filaments were placed in specially constructed glass aerosol bottles, filled with water, and heated in a laboratory oven.

Photographs were also made of filaments sealed with water in specially constructed glass tubes also placed in the oven

FIGURE 6.1. - HIGH SPEED STILL PHOTOS

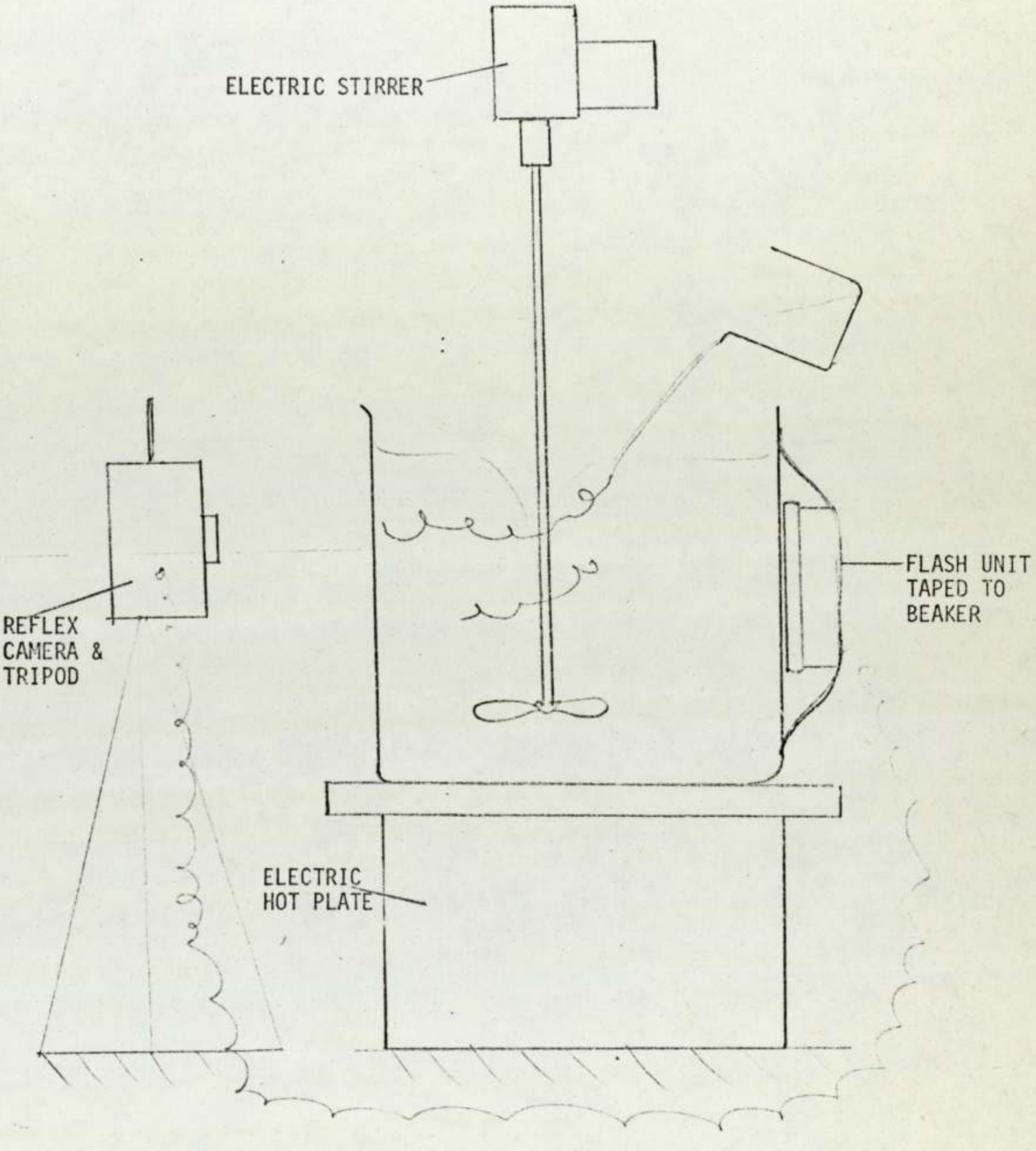


FIGURE 6.2. - HIGH SPEED CINE PHOTOGRAPHY

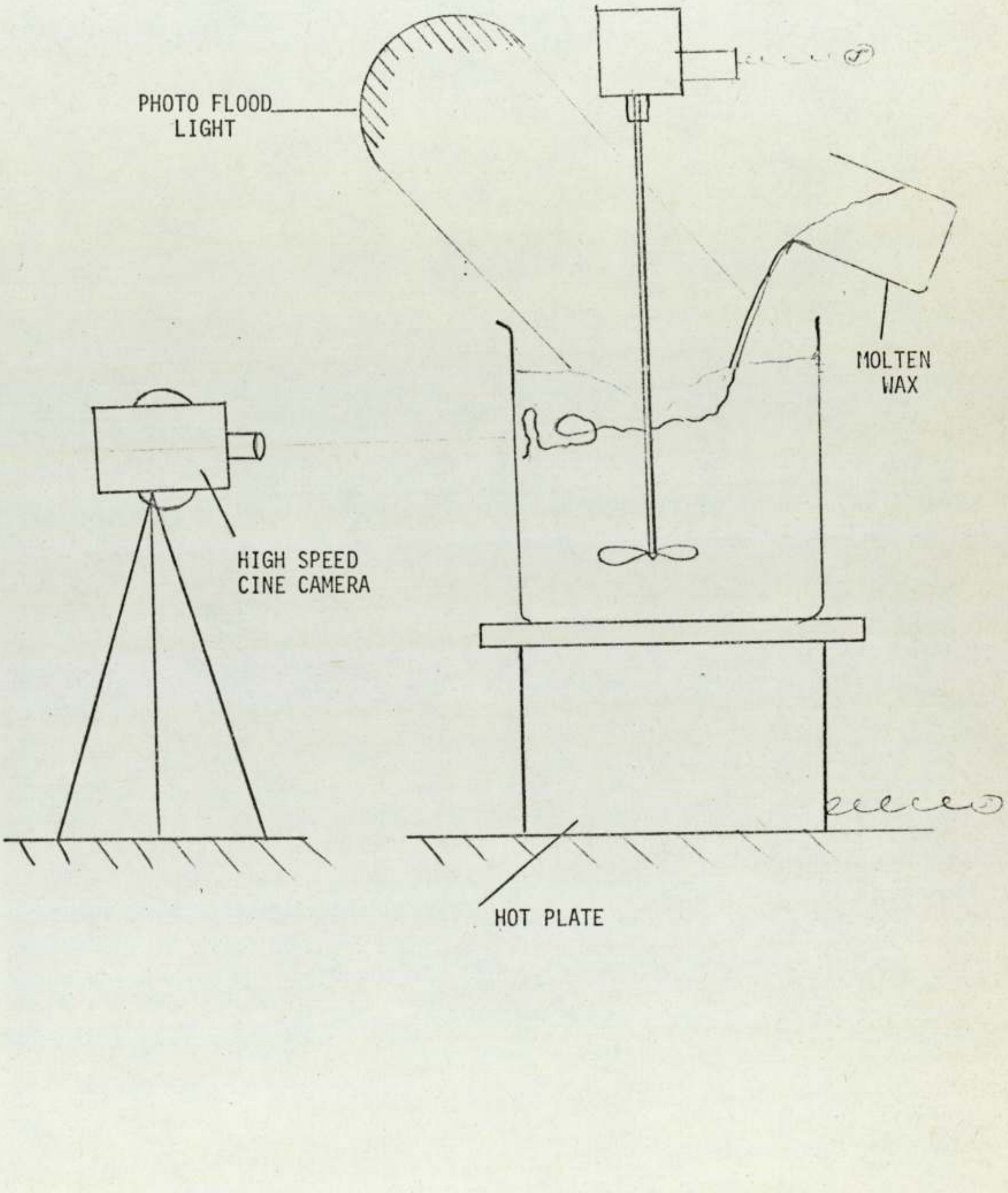
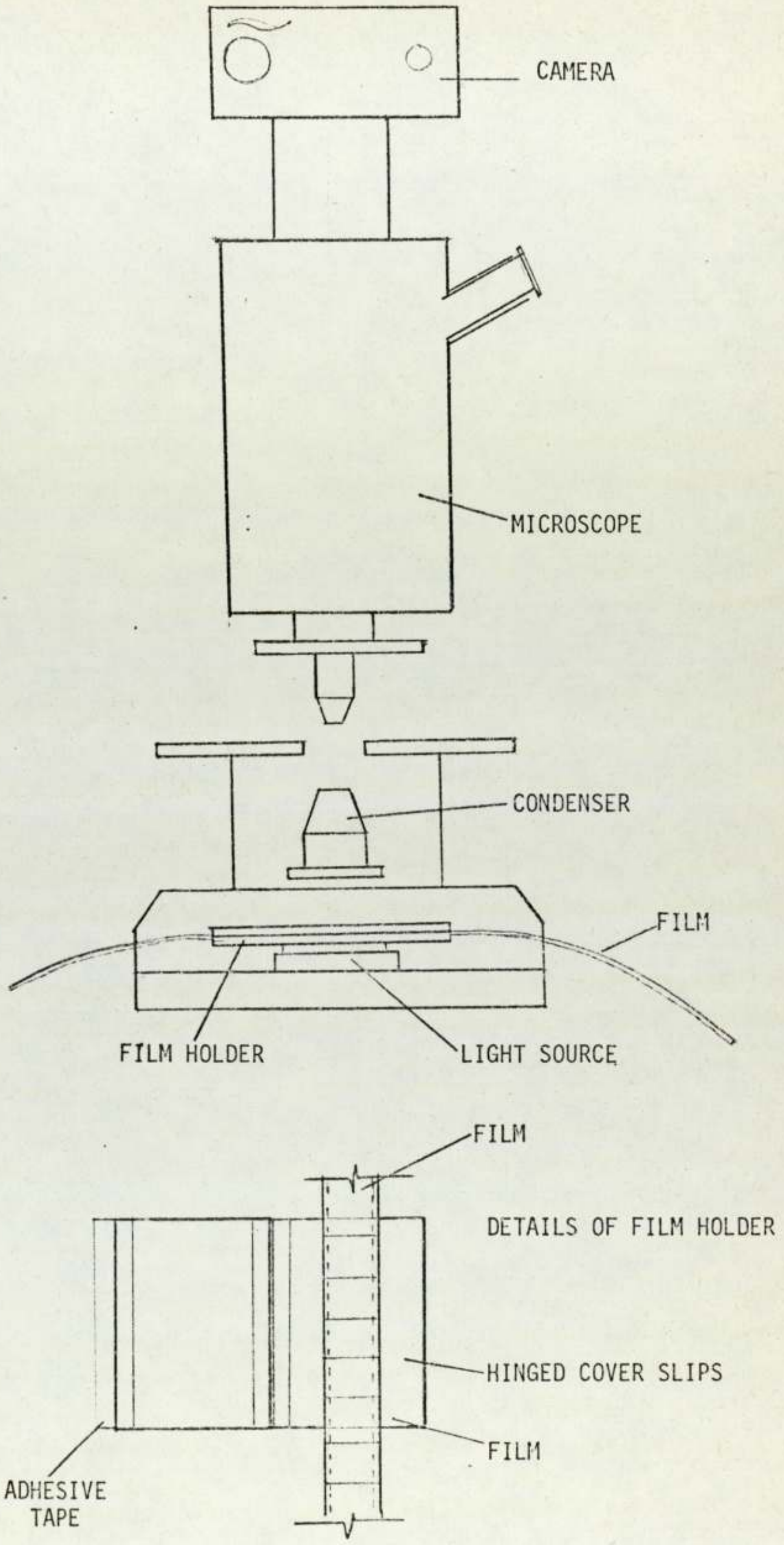


FIGURE 6.3. - PRODUCTION OF PRINTS FROM CINE FILM



and removed periodically for inspection.

6.3.4. Apparatus for Dynamic Emulsification.

The apparatus for these experiments is shown in Figure 6.4. It consisted of a metal container equipped with a bottom outlet surrounded by a heating mantle. As shown in Figure 6.4., the container was filled with water which was heated and fed via the rubber tubing through the test cell containing the solidified wax filament. After passing over the filament, the water passed to a collection vessel. Flow rates through the apparatus were determined by weighing and stop watch, and the emulsification of the filament observed by microscope. The extent of emulsification was determined gravimetrically.

6.4. Experimental Techniques.

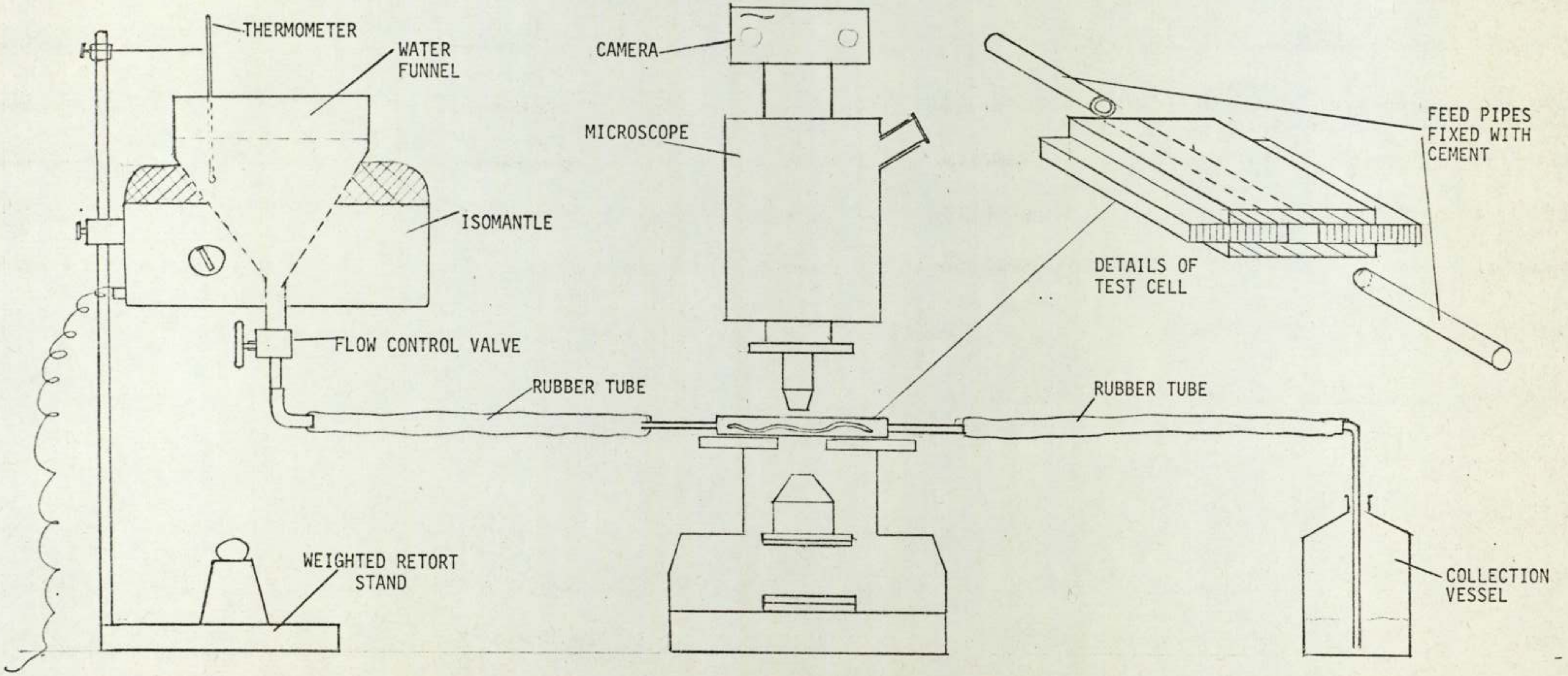
6.4.1. Visual Examination of Wax Emulsification.

Using the standard formula but with dye added to the wax melt, the process of wax emulsification by surface addition was observed closely. Further details of the behaviour of the molten wax stream were gained by deliberately lowering the water temperature to 20°C, when the wax stream literally 'froze' enabling its removal and examination.

6.4.2. High Speed Photography (Stills).

Further evidence on the behaviour of the dyed wax stream

FIGURE 6.4. - DYNAMIC EMULSIFICATION APPARATUS



during the emulsification process was gathered via a series of high speed photographs. These were taken under standard conditions of emulsification using a reflex camera focused onto a strip of wire of similar dimensions to the wax stream placed at and below the water surface. Illumination was provided by an electronic flash unit strapped to the side of the emulsion vessel (a glass beaker). Photographs were taken looking down on the water surface and through the sides of the glass beaker to examine the activity of the wax stream below the water surface.

6.4.3. High Speed Photographs (Cine).

In order to see the whole process, it was decided to make a number of high speed cine films using standard conditions of emulsification but with dyed wax for greater definition. This was achieved by a similar technique to that used for the still photographs detailed under 6.4.2. above. Two operators were again necessary, one to pour molten wax into the emulsion vessel and the other to operate the camera. Films were taken at various speeds between 300 and 1200 frames per second. Once again, the camera was pre-focused according to the suppliers manual, using special film provided and a piece of wire of similar dimensions to the wax stream which was held below the water surface.

Illumination was provided by a single photo-flood lamp mounted behind the emulsion vessel, providing illumination through it. The glass emulsion vessel was mounted on an electric hot plate in order to allow the camera complete access to the vessel sides. The arrangement is shown in Figure 6.2.

Films were made of the molten wax initially hitting the water surface and at various points below the surface. Agitator speeds were varied slightly and a film was made using baffles installed in the emulsion vessel. The camera had to be started almost immediately the wax impacted the water, initiated by a verbal command from the operator pouring it. An additional reason for immediate activation of the camera was the opacity which rapidly developed in the beaker as the emulsification process proceeded.

Each film was run through an editing projector and selected frames printed on a 7¼ cm x 9cm format for detailed examination and reproduction in this dissertation. These are shown in Section 6.4.5.

6.4.4. Techniques for Investigating Spontaneous Emulsification.

It was deduced from the above films that the mechanism proceeded via wax filaments in turn formed by impacting the molten wax with moving water. Therefore further experiments were conducted using wax filaments. During this work, filaments were prepared by using a standard wax melt incorporating saponified wax, emulsifier and dye; and pouring it into the water at ambient temperatures. Applying standard agitation produced filaments of roughly 1 mm in diameter.

These filaments were then placed in specially constructed glass aerosol bottles and raised to 95; 100; and 120°C. The time to effect emulsification and the extent of this process wax measured in each case during static conditions. Several filaments were also encapsulated in special sealed tubes (See Figure 6.5.), complete with water and, after raising to 120°C, examined for signs of emulsification. Similar experiments were undertaken using a Beeswax emulsion detailed in Table 6.1. Photographs were used to provide a suitable record of events with time.

6.4.5. Dynamic Emulsification.

Using filaments prepared as described in 6.4.4. above, a cell was constructed as shown in Figure 6.4. This unit held a pre-weighed filament over which water passed at up to 100°C. Because the wax was only heated by the water flowing over it and in order to slow down the process for photography, a low

TABLE 6.1.

FORMULA FOR BEESWAX EMULSION

INGREDIENT	PURPOSE	% W/W
Refined Beeswax	To form emulsion.	16.59
Potassium hydroxide 50% w/w.	To saponify wax and form part of emulsifier system.	0.60
Ethoxylated Linear alcohol (Tergitol 15-S-9)	Emulsifier (nonionic surfactant.	3.11
Ethylene Glycol	To reduce the viscosity of the wax melt.	0.85
Mains water	Diluent.	78.65
Formaldehyde (37% w/w)	Bactericide	0.20
		100.00

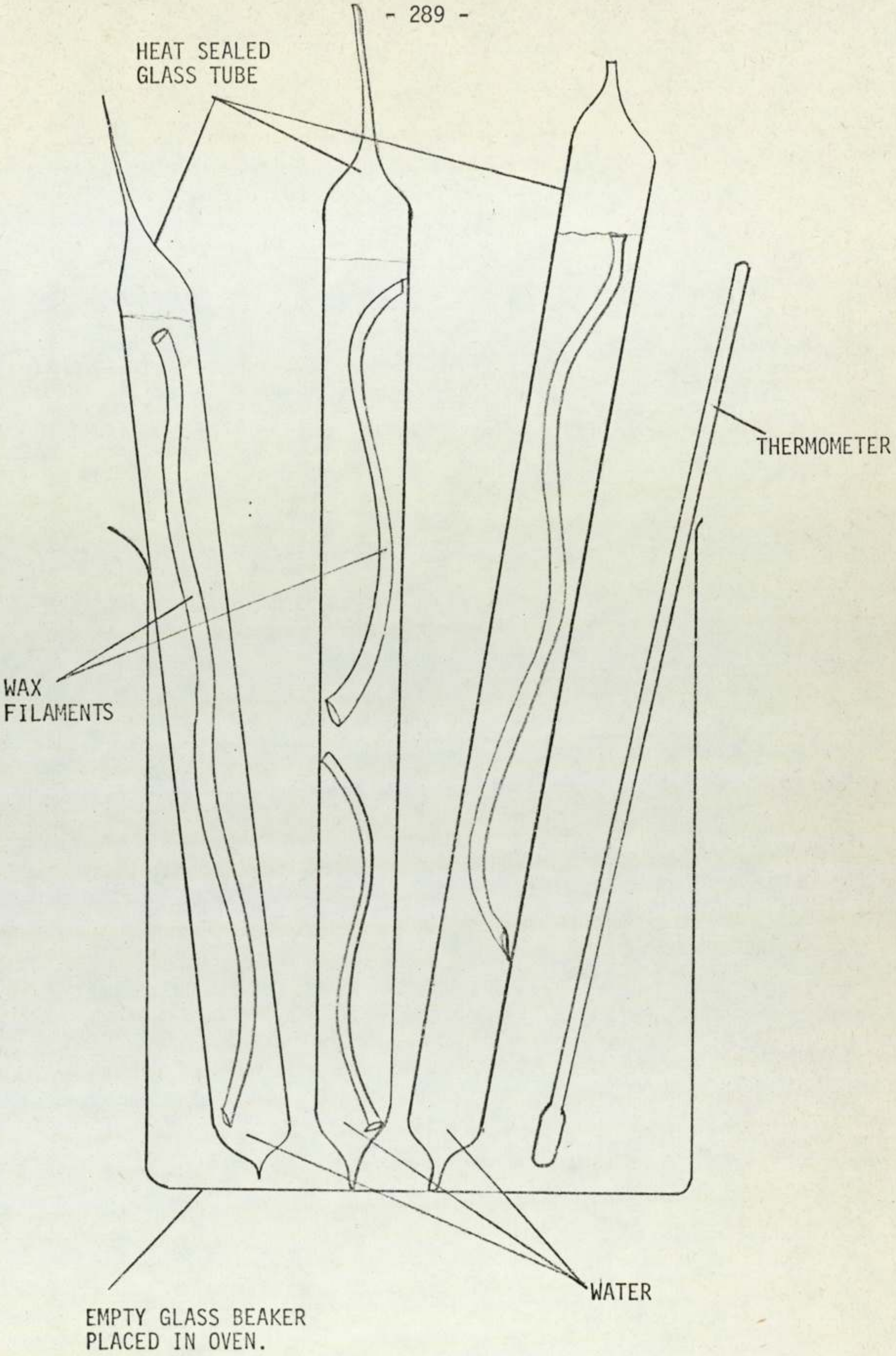


FIGURE 6.5. - SPONTANEOUS EMULSIFICATION TEST TUBES

melting point Beeswax was used to ensure the wax would melt (see Table 6.1.). The process of emulsification was followed by photomicrography. The extent of emulsification was measured gravimetrically and related to water flow rates. The resultant emulsions were subject to quality assessment techniques.

6.4.6. Work Done in Producing Emulsion Droplets.

(a) Theoretical Considerations.

When a typical wax emulsion is produced, the volume of molten wax is broken up into millions of microscopic and submicroscopic particles. The action of transforming a bulk liquid mass into small particles requires the expenditure of energy in order to overcome intermolecular forces tending to hold the liquid mass together. In fact the dispersion of the liquid wax or oil phase as droplets increase the interfacial area between oil (or wax) and water by a large extent. This in turn leads to an increase of the surface free energy according to the relation:-

$\Delta F = \gamma \Delta A$ where

ΔF = The increase in surface free energy in ergs.

γ = The interfacial tension in dyne/cm between the molten wax and the emulsification water.

ΔA = The increase in surface area effected by disrupting the oil (wax) phase into droplets.

The increase in free energy must come from external sources, i.e., work must be done on the system. This in the case of the process under study, is achieved via the agitator. Therefore in addition to pulling the wax below the water surface the agitator must cause sufficient shear forces to act on the wax to enable the interfacial tension forces to be overcome. When this occurs, then both ΔA and ΔF can increase via particulate formation. Therefore

ΔF = Energy to be supplied by the agitator.

Consequently it should be possible to compare the ΔF for a given wax feed rate and particle size, with the power theoretically obtainable from the agitator and investigate the criticality of stirrer speed from the viewpoint of droplet formation. Such an exercise is completed in Sections (b) and (c) below.

(b). Calculation of Work Done in Droplet Formation.

From the studies completed in Section 4, it was concluded that most of the particles in a wax emulsion are less than 1 micron. For the purpose of this calculation, it will be assumed that the mean particle diameter is 0.75 microns.

Using the laboratory apparatus and standard formula and process, wax is added to the emulsion water at approximately

53 g/minute

i.e. 53 grams of wax or $57.9 cm^3/min$ = $\underline{\underline{0.96 cm^3/sec}}$

Volume of wax particles having a diameter of 0.75 microns

$$= \frac{\pi D^3}{6} = \frac{\pi\ 0.75^3}{6 \times 10^{12}} = \underline{\underline{\frac{0.221}{10^{12}}\ cm^3}}$$

$$\text{No of particles produced/sec} = \frac{0.96 \times 10^{12}}{0.221} = \underline{\underline{4.344 \times 10^{12}}}$$

Surface Area of 0.75 micron wax particles

$$= \pi D^2 = \frac{\pi \times 0.75^2}{10^8} = \underline{\underline{\frac{1.767}{10^8}\ cm^2}}$$

Total surface area afforded by 0.75 micron particle

$$= 4.344 \times 1.76 \times 10^4 = \underline{7.645 \times 10^4}\ cm^2 = \Delta A$$

To a good approximation, this is all new surface.

The interfacial tension between the molten wax and water could not be measured in the case of the AC540 material due to the need to operate under pressure. Instead measurements were made with the substitute Beeswax emulsion (see Table 6.1.) using a du Nouy tensiometer. Fortunately the surface tension of the wax alone (i.e. without emulsifier) was similar to that reported for AC540 (76) at 30 dynes/cm.

The measured interfacial tension at the Beeswax/water interface using emulsifiers was 2.5 dynes/cm at 95°C. This value was assumed to be close to the value likely to be reached with the study emulsion.

i.e. γ = 2.5 dynes/cm.

Therefore $\Delta F = 2.5 \times \Delta A$

$= 2.5 \times 7.645 \times 10^4$ ergs/sec.

$= \underline{\underline{19.114 \times 10^4 \text{ ergs/sec}}}$.

<u>OR</u>

Energy required to produce wax particles at 0.75 microns

$= \underline{\underline{19.91 \times 10^4 \times V_w \text{ erg/sec.}}}$

Where V_w = Wax volumetric feed rate in cm^3/sec

The above relationship was used to compute the energy requirements for various wax feed rates which are plotted in Figure 6.6.

Thus

F_{50} = energy required @ feed rate of 50g/min = 18.100x10^4ergs/sec

F_{500} = energy required @ feed rate of 500g/min = 181.00x10^4 ergs/sec

F_{1000} = energy required @ feed rate of 1000g/min = 3.62x10^4ergs/sec

(c) Estimation of Total Energy Available from Agitator.

The method used followed the procedure of Rushton (146) which involves the following steps:-

(i). The calculation of the Reynolds number.

(ii). Reading the power function from the graphical data of Rushton.

(iii). Calculation of the Froude number and its exponent from Rushton's tables.

(iv). Calculation of the power applied to the emulsion water via the propeller.

The individual steps will now be described in detail.

(i). Calculation of Reynolds Number.

N_{Re} = Reynolds Number = $\frac{Da^2 n \rho}{\mu}$

Where Da = agitator diameter = 4.5cm

n = revolutions/sec = $\frac{1000}{60}$ = 16.7 for the standard process.

ρ = density of wax emulsion = $1 g/cm^3$ at $95^{o}C$

μ = viscosity of wax emulsion = 2.5 cps at $95^{o}C$ (measured by Brookfield viscometer)

$$N_{Re} = \frac{Da^2 n}{\mu} = \text{const} \times n = \underline{\underline{810n}}$$

(ii). Obtaining the Rushton Power Function.

This may be obtained from Figure 13 in Rushton's paper (146) which plots N_{Re} as abscissa and power function as ordinate.

Hence:-

Speed rpm	=	1000	400	300
n	=	16.7	6.7	5
N_{Re}	=	13527	5427	4050
Power function ($\emptyset$)	=	0.65	0.7	0.78

(iii). Calculation of the Froude Number and its Exponent.

From Table 4 in Rushton's paper (146), the Froude number exponent may be calculated from the relation.

$$m = \frac{a - \log N_{Re}}{b}$$

$$\text{where} \quad \left. \begin{aligned} a &= 2.6 \\ b &= 18.0 \end{aligned} \right\} \text{ for laboratory apparatus.}$$

Thus using the values of N_{Re} calculated above the following data was obtained:-

Speed	1000	400	300
N_{Re}	13527	5427	4050
m	-0.0851	-0.063	-0.0556

The Froude number is given by:-

$$N_{Fr} = \frac{n^2 Da}{g}$$

where g = acceleration due to gravity = 981cm/sec/sec

Da = agitator diameter = 4.5cm

n = revs per second.

Therefore:-

$$N_{Fr} = \frac{4.5 n^2}{981} = \frac{4.592\ n^2}{10^3}$$

Hence for the speeds already examined:-

Speed rpm =	1000	400	300
N_{Fr} =	1.281	0.206	0.115
N_{Fr}^{m} =	0.979	1.105	1.128

(iv). Calculation of Power Applied to Emulsion Water.

As demonstrated by Rushton:

$$P = \emptyset N_{Fr}^{m} n^3 Da^5$$

Where P = power applied to emulsion water - ergs/sec

all other symbols as previously defined.

Therefore at the speeds examined

$$P_{1000} = 0.65 \times 0.979 \times 16.7^3 \times 4.5^5 \times 1 = 5,469,057 \text{ ergs/sec.}$$

$$P_{400} = 0.7 \times 1.105 \times 6.7^3 \times 4.5^5 \times 1 = 447,689 \text{ ergs/sec.}$$

$$P_{300} = 0.78 \times 1.129 \times 5^3 \times 4.5^5 \times 1 = 203,126 \text{ ergs/sec.}$$

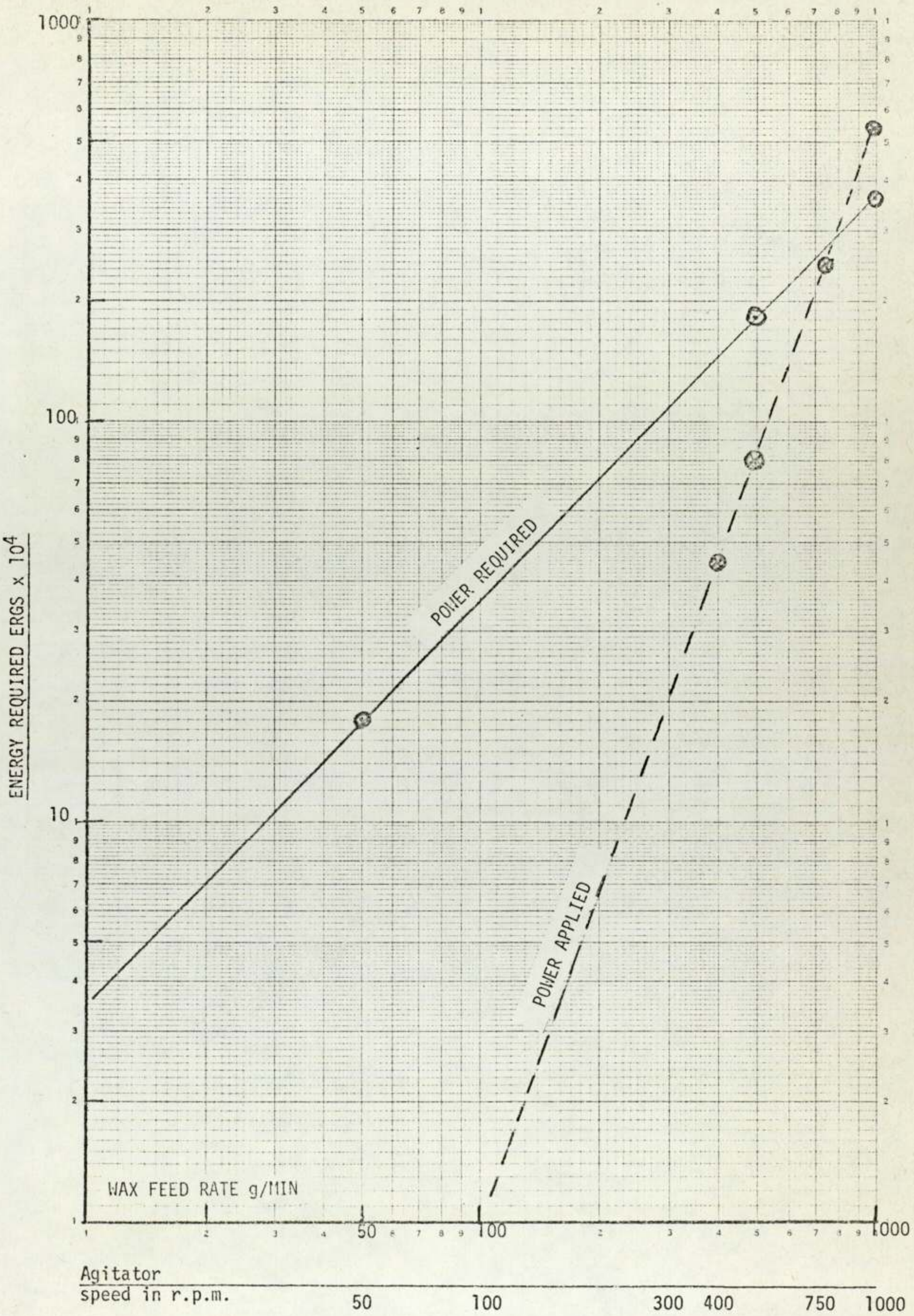
The above calculations were similarly completed for other agitator speeds and are summarised in Table 6.2. and graphed in Figure 6.6.

TABLE 6.2.

SUMMARY OF DIMENSIONLESS GROUPS AT VARIOUS SPEEDS

Speed rpm	1000	750	500	400	350	300	250
Speed rps	16.7	12.5	8.3	6.7	5.8	5	4.2
N_{Re}	13,527	10,125	6,723	5,427	4,698	4,050	3,402
ϕ	0.65	0.66	0.70	0.73	0.75	0.78	0.80
N_{Fr}	1.281	0.718	0.316	0.206	0.155	0.115	0.081
m	-0.085	-0.078	-0.068	0.063	-0.060	-0.056	-0.052
${N_{Fr}}^{m}$	0.979	1.026	1.082	1.105	1.118	1.129	1.140
Calculated Power P_{-1} erg/sec^{-1}	5,469,057	2,440,553	799,147	447689	301,894	203126	124,684

FIGURE 6.6. - ENERGY REQUIREMENT FOR EMULSIFICATION AT VARIOUS FEED RATES



6.5. Results.

6.5.1. High Speed Photographs of Wax Emulsification.

Plates 6.1. to 6.3. show the preparation of a wax emulsion in various stages of completion. The molten wax may be identified by its pinkish colour as a result of incorporated dye. Solidified wax has a white opaque appearance. Plate 6.4. shows the method of addition and Plate 6.5., the close-up of the water surface showing the molten wax stream and the vortex created by the stirrer.

Plate 6.6. shows emulsification when the water temperature is too low. As may be seen from this photograph, when this occurs, wax solidifies on the surface prior to emulsification. This leads to fragments and other unemulsified wax particles being suspended in the water without emulsification.

A further set of photographs taken below the water surface are shown in Plates 6. 7 , 6. 8, 6. 9. and 6.10.. Plate 6.7 . shows the condition at the start with the stirrer turning and in the top right hand corner, molten wax first impacting the water surface. The next two photographs (Plates 6.8. and 6.9.) show the molten wax filament being dragged below the water surface and exhibiting its convoluted movements prior to emulsification. Plate 6.10. shows how relatively large amounts of air can be pulled into the water via the agitator vortex, at high agitation rates.

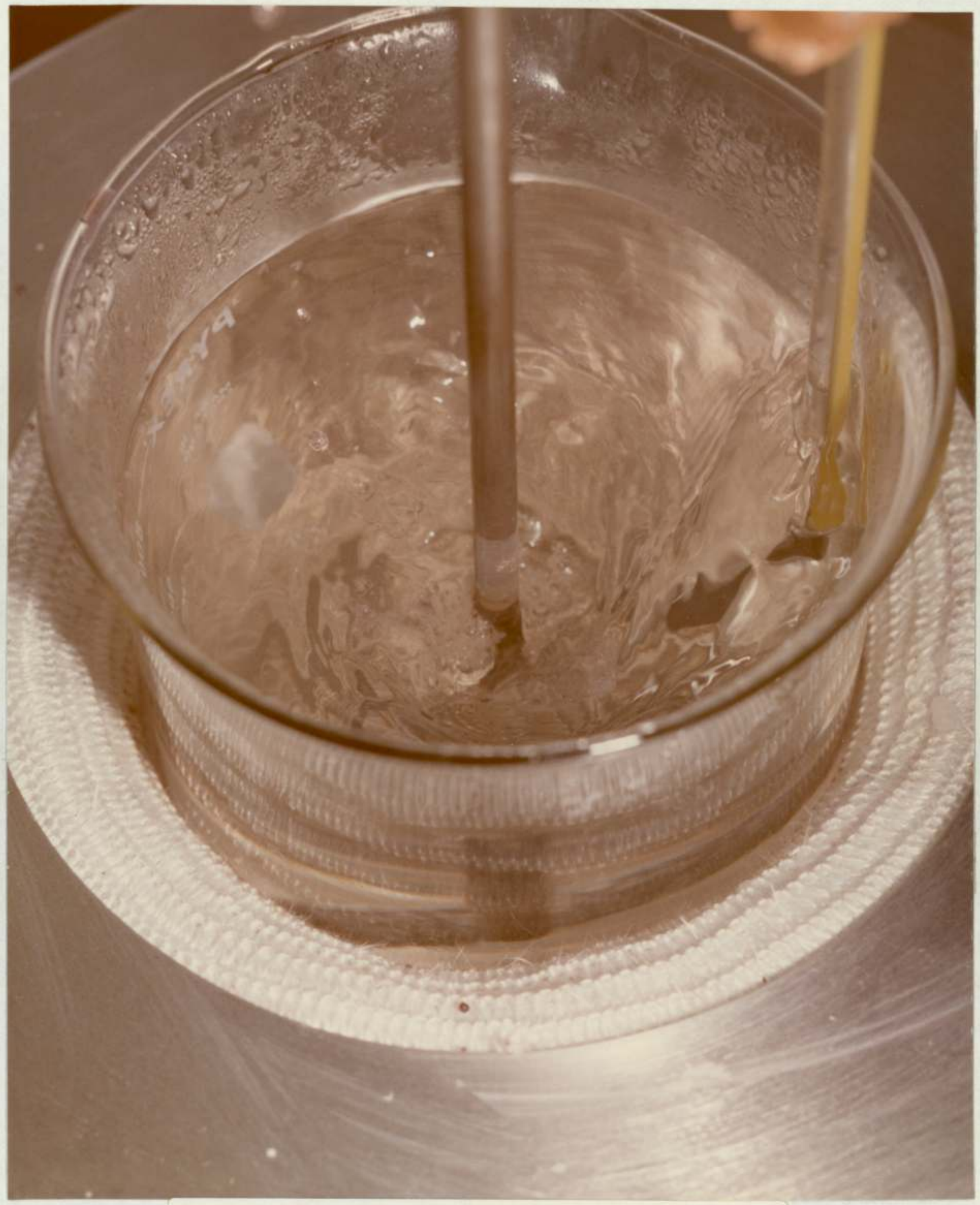


PLATE 6.1.

The Emulsification of Wax

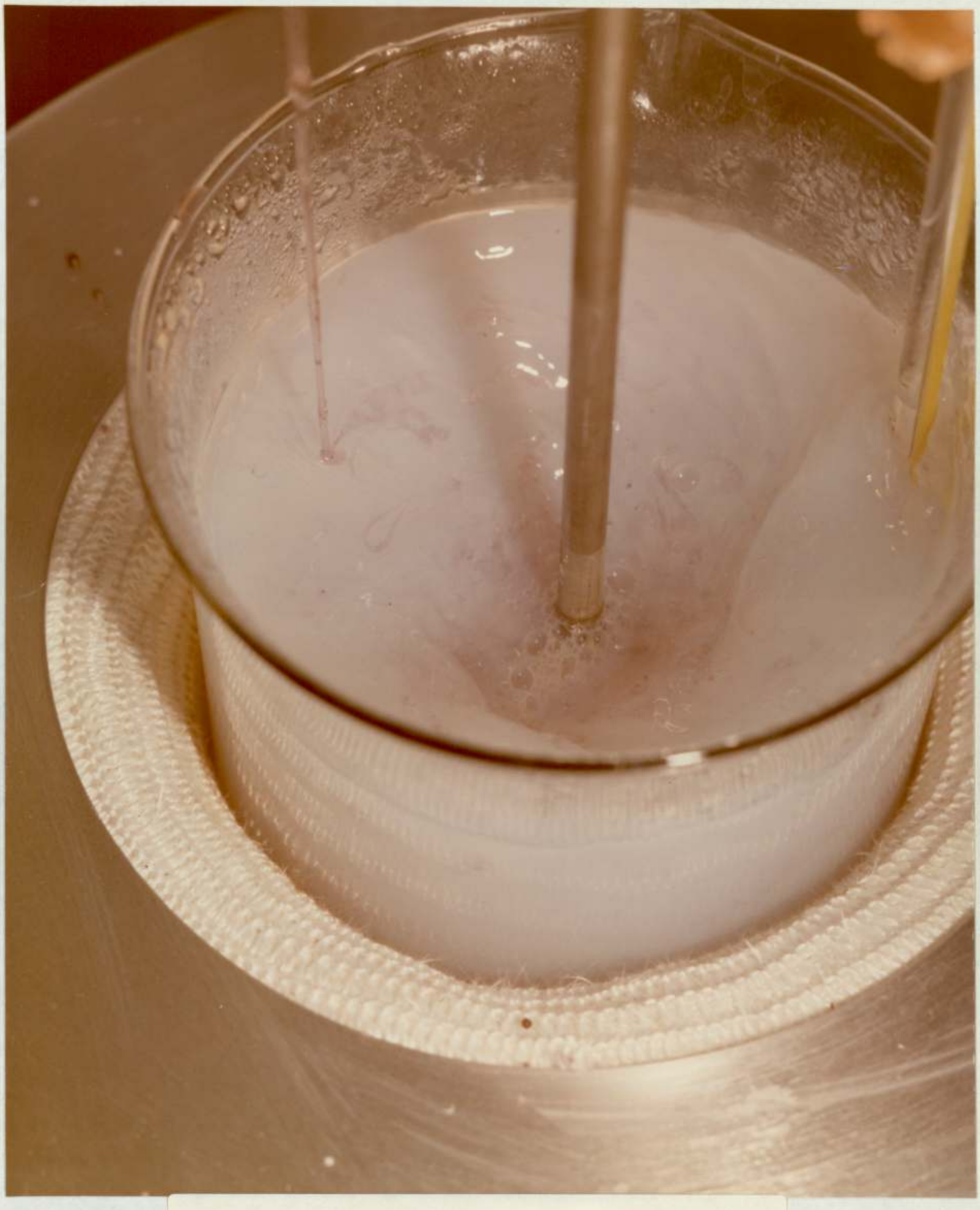


PLATE 6.2.

The Emulsification of Wax

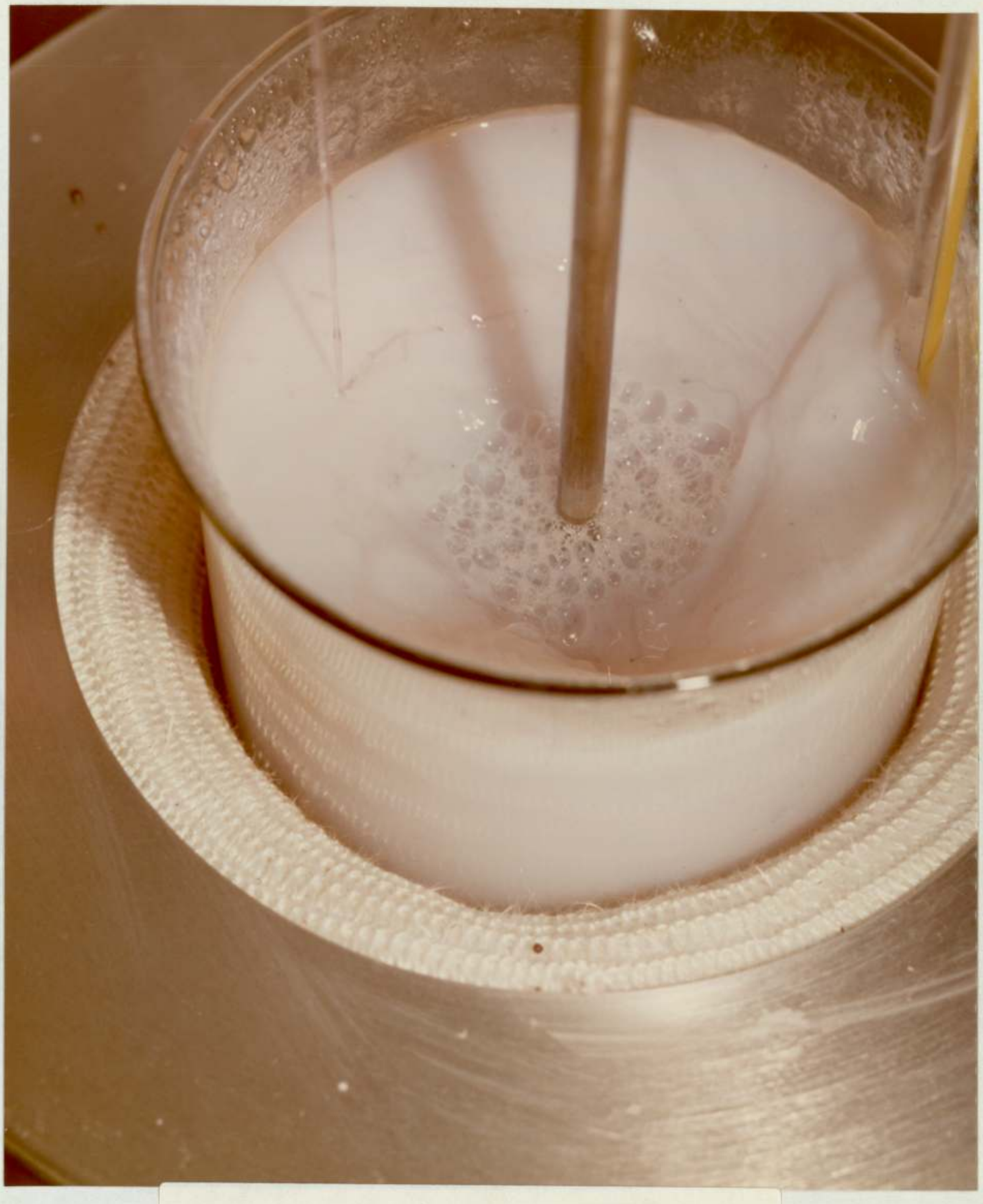


PLATE 6.3.

The Emulsification of Wax

PLATE 6.4.

The Emulsification of Wax

PLATE 6.5.

The Emulsification of Wax

PLATE 6.6.

The Emulsification of Wax

PLATE 6.7.

The Emulsification of Wax

PLATE 6.8.

The Emulsification of Wax

PLATE 6.9.

The Emulsification of Wax

PLATE 6.10.

The Emulsification of Wax

Plate 6.11. shows the situation where no agitation exists. Molten wax has been poured onto the water surface where it lays in a molten agglomerated mass. Plate 6.12. shows the situation when this mass is moved gently with the agitator shaft. As may be seen, emulsification occurs immediately.

Finally, Plate 6.13. shows the method of preparation of wax filaments for study as described in Section 6.4.4.

6.5.2. Results of Spontaneous Emulsification Experiments.

Plates 6.14. and 6.15. show the arrangement for examination of spontaneous emulsification. In plate 6.14., the experiment is just about to begin with the filaments contained in the glass aerosol bottle (able to stand pressures up to 100 p.s.i.g.) filled with water and placed in the oven pre-set at 120°C. Plate 6.15. shows the situation after 1 hour, 24 hours, 168 hours and 1000 hours, i.e. no change. Plate 6.16. shows the result when the bottle is slightly shaken.

Plate 6.17. shows the resultant emulsion produced when a magnetic stirrer bar was included in the aerosol bottle along with the wax and water. In these cases, emulsions were formed by withdrawing the bottle from the oven and placing it on the stirrer unit and thus providing vigorous agitation. Plate 6.17. shows an 'emulsion' formed when the wax was not fully molten due to insufficient time in the oven (less than 1 hour).

PLATE 6.11.

The Emulsification of Wax

PLATE 6.12.

The Emulsification of Wax

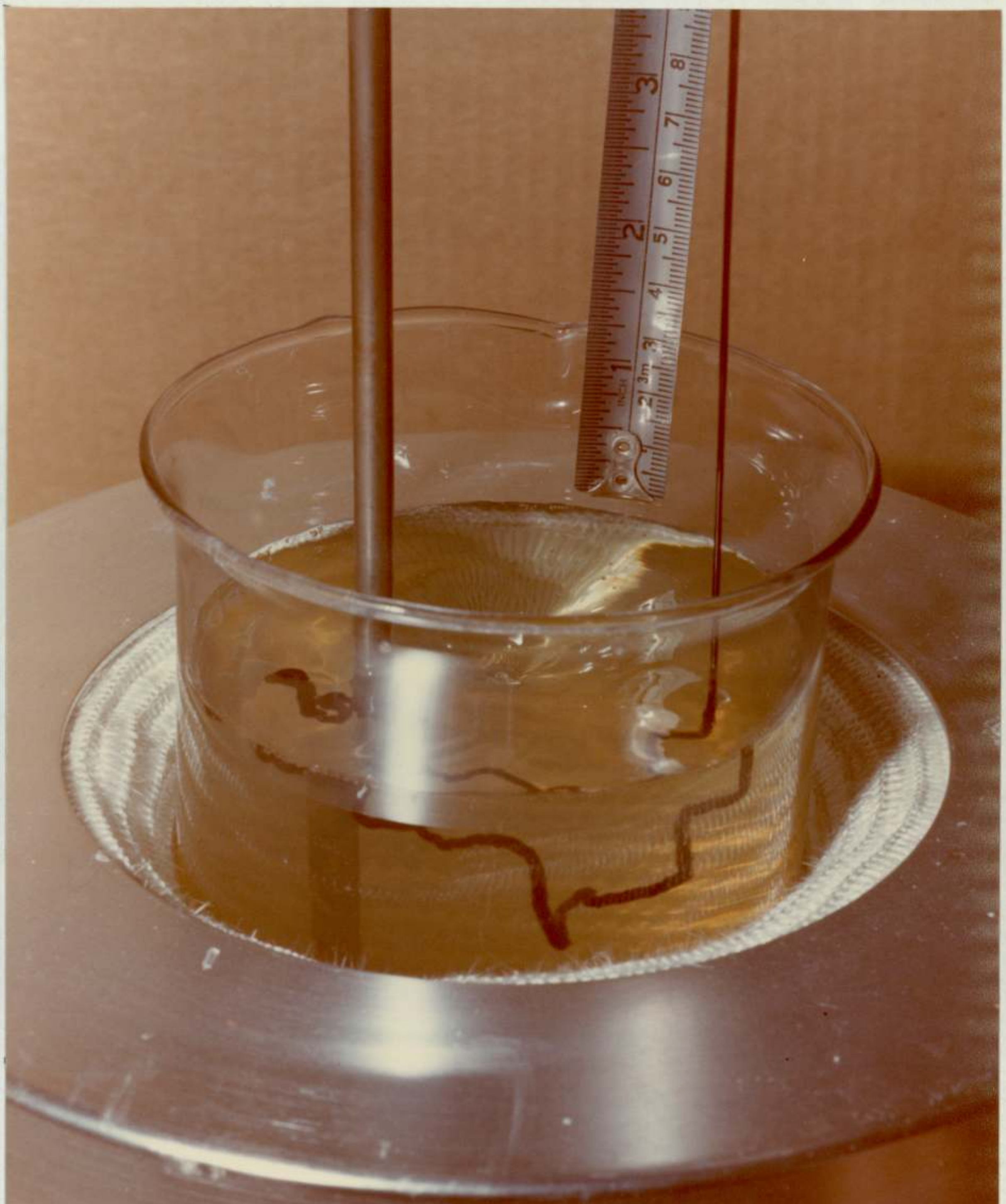


PLATE 6.13.

Preparation of Wax Filaments for Further Study

PLATE 6.14.

Spontaneous Emulsification Experiment

PLATE 6.15.

Spontaneous Emulsification Experiment

PLATE 6.16.

Spontaneous Emulsification Experiment

PLATE 6.17.

Malformed Pressure Emulsion

Plates 6.18. and 6.19. show wax filaments encapsulated together with water in sealed tubes. Plate 6.18. shows the start of the experiment and plate 6.19. after one hour and 24 hours in the oven at 120°C.

6.5.3. Experiments on Dynamic Emulsification.

Plate 6.20. shows the dynamic emulsification test cell with the wax filament mounted in place. Table 6.3. shows the variation between water temperature, water flow rate and emulsification time. In these experiments, the stop watch was started as soon as emulsifcation was seen to occur. The water flow rate was determined separately also using a stop watch. Plates 6. 21, 6. 22, and 6. 23 show the sequence of the emulsification of a wax filament, beginning with the undisturbed wax water interface which disrupts into spherical droplets on the application of shear via hot water flow. Plate 6. 24 shows the formation of wax fragments when the filament skin is not completely liquid.

Plate 6.25. to 6.28. are prints from the high speed cine films which show the formation of wax filaments.

6.6 Discussion.

From the results shown in 6.5.1., it was clear that in order for emulsification to occur, the wax needed to be molten or in the liquid phase. If this were not so, then unemulsified particles resulted.

High speed still and cine photographs indicated that

TABLE 6.3. - RATE OF EMULSIFICATION

RUN NUMBER	WT OF WAX FILAMENT	TIME TO EMULSIFY SECS	VOLUME OF WATER cm3	LINEAR FLOW RATE CM/SEC	RATE EMULSIFICATION g/MIN	TEMPERATURE °C
1	0.1944	389	413	5.4	0.03	78
2	0.2792	239	540	11.5	0.07	79
3	0.1683	32	169	26.9	0.32	80
4	0.2241	20	145	37.0	0.67	80
5	0.2071	17	147	44.0	0.73	80
6	0.2021	110	104	4.8	0.11	95
7	0.1984	12	30	12.3	0.99	94
8	0.1553	6	27	22.5	1.55	94
9	0.3016	← Emulsification too fast to measure →		>22.5		93
10	0.2817	19	56	15.0	0.89	94

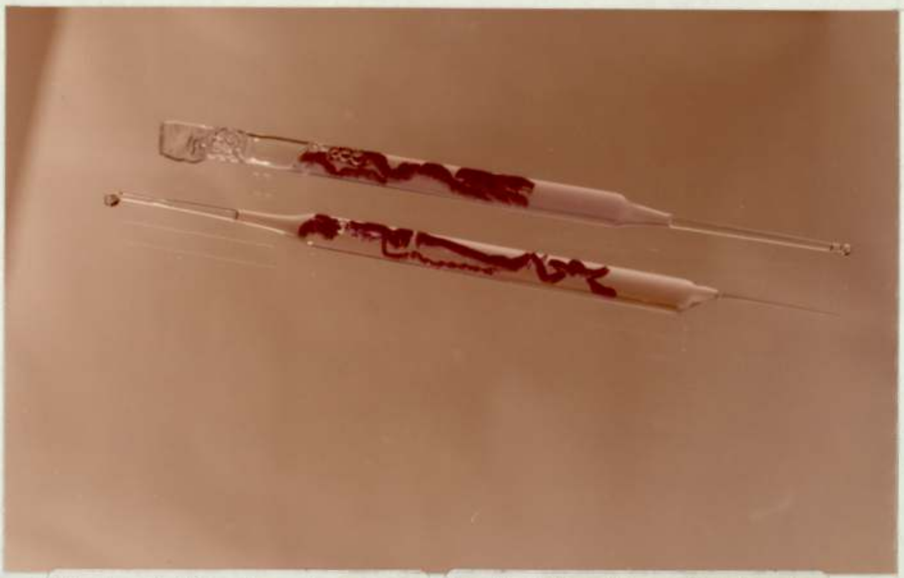


Plate 6.18 Spontaneous Emulsification @ start

Plate 6.19. Spontaneous Emulsification @ 24 hrs

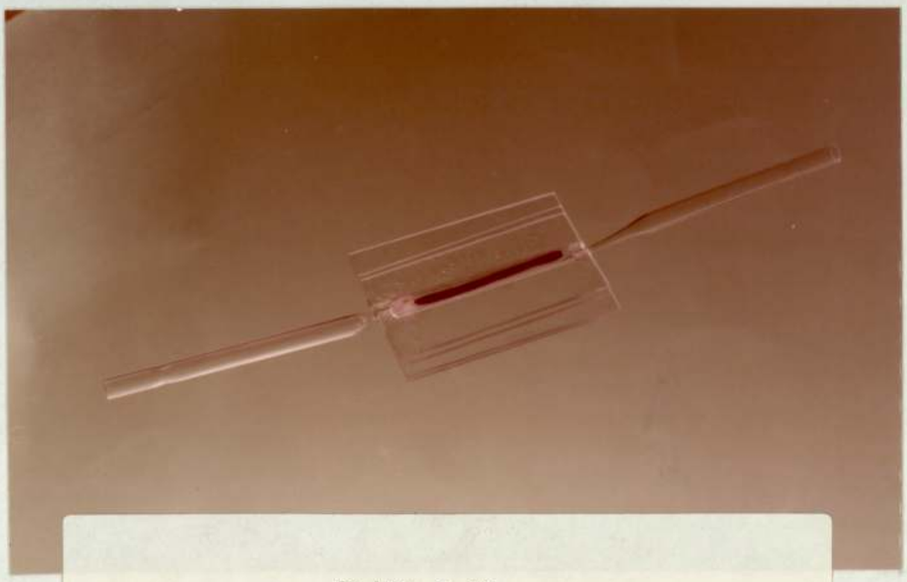


PLATE 6.20.

Dynamic Emulsification Experiment
(Test Cell)

PLATE 6.21.

Dynamic Emulsification of Wax Filament

50 x Magnification

PLATE 6.22.

Dynamic Emulsification of Wax Filament

500 x Magnification

PLATE 6.23.

Dynamic Emulsification of Wax Filament

500 x Magnification

PLATE 6.24.

Dynamic Emulsification of Wax Filament

125 x Magnification

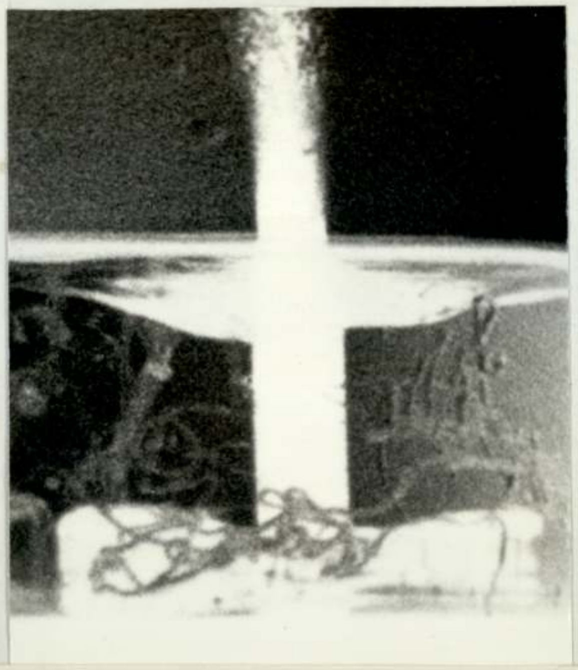


PLATE 6.25.

Print From High Speed Cine Film

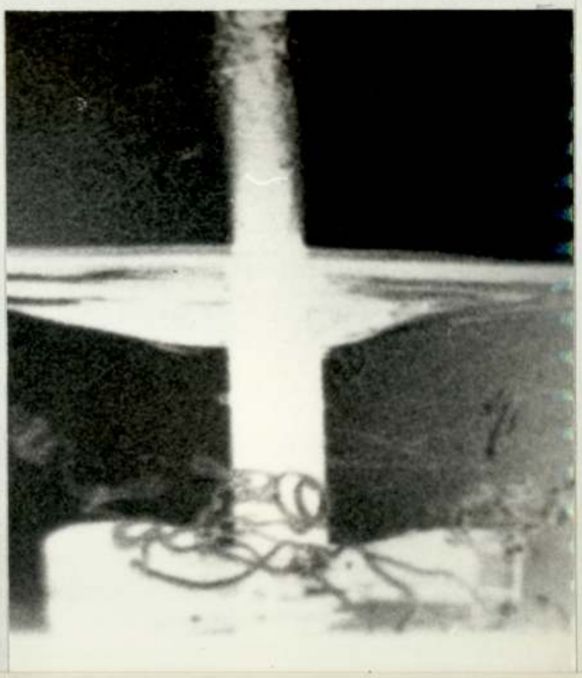


PLATE 6.26.

Print From High Speed Cine Film

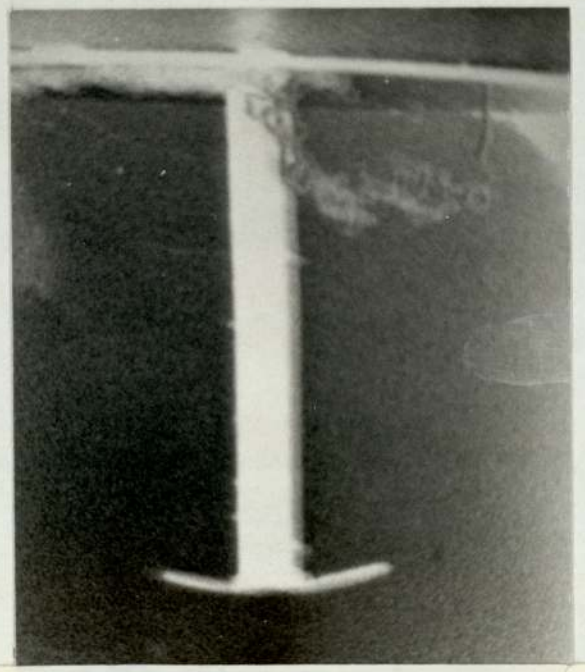


PLATE 6.27.

Print From High Speed Cine Film

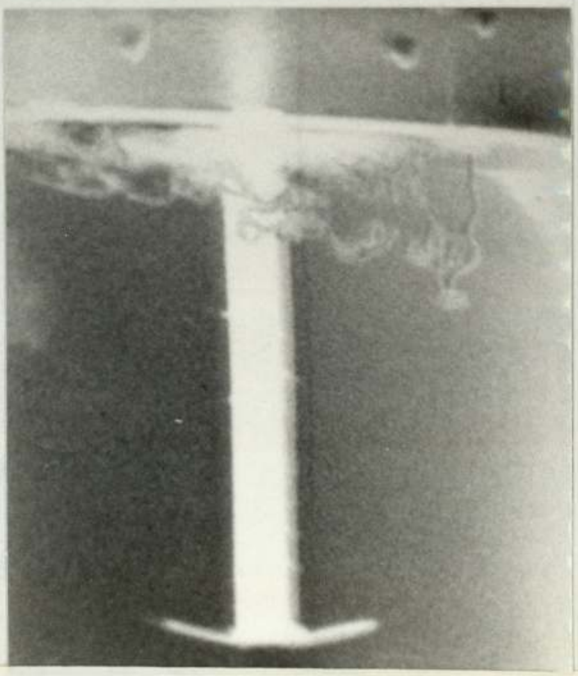


PLATE 6.28.

Print From High Speed Cine Film

emulsification occurred via a wax filament, sometimes continuous, sometimes broken, which moved below the water surface in a convoluted manner coiling about itself, the agitator blades and to some little extent the agitator shaft. At some point, this filament disintegrated into emulsion size particles. However, on a macroscopic scale, it was difficult to see how and when this occurred. The high speed cine photographs made it quite clear that it was not the agitator which was the main contributor to filament break up. For although the agitator was seen to break filaments into several large pieces, droplet formation was thought to be by some more complex mechanism.

Finally, the visual experiments indicated that if molten wax were allowed to lie on the water surface in a static condition, emulsification would not occur. In such a case, the wax would rapidly cool, solidify, and merely lie there as a solid lump. Simple movement with an agitator shaft or suitable object produced immediate emulsification provided that the wax was still molten. These experiments further emphasised the need for the agitator system to drag the molten wax below the water surface (as quickly as possible) in order to allow maximum wax/water contact in a more turbulent regime, and minimise the cooling rate of the wax.

The experiments on spontaneous emulsification made it clear that to produce a satisfactory emulsion, the wax must be molten and in a state of rapid movement. The static filaments in these experiments emulsified very slowly and to little extent while in the static condition. This was even true at fairly high temperatures e.g. up to 120°C, when all the wax should be molten. However, even simple hand shaking under these conditions produced rapid emulsification, verifying the need to cause the water to stream over the wax filament. The complete emulsification of the filaments was demonstrated by the use of a magnetic stirrer previously included in the glass bottle.

The dynamic emulsification experiments illustrated the way in which wax particles were formed by the application of shear. These particles were seen to be microscopic and spherical during normal emulsification conditions i.e. when the wax was molten but irregular shaped and macroscopic when the wax filament was semi-solid. These experiments further illustrated two of the critical requirements for the satisfactory emulsification of wax namely:-

(i) Liquid/Liquid contact.

(ii) The application of disruptive shear forces to the filament outer skin.

Because the water medium was usually at 10 - 15°C below the wax temperature, (See Section 3), it was clear that droplet formation must occur rapidly otherwise the wax would solidify and subsequently large irregular fragments would result. As the process of emulsification had been shown to occur from the outer skin of a wax filament, which in turn was subject to the greatest cooling, the criticality of rapid disruption of the wax was emphasised. If cooling and subsequently solidification of the filament skin could occur prior to its disruption into droplets, then emulsification was impossible. This mechanism appeared to explain why a wax having a melting point above approximately 110°C could not be emulsified by atmospheric techniques.

6.7. Conclusions.

(a). The mechanism of wax emulsification by the atmospheric surface method is that of filament formation followed by subsequent erosion from the filament outer skin inwards.

(b). The transformation of molten wax filaments into emulsified spherical particles is effected by shear forces which are induced by differential velocities between the wax filaments and the surrounding water.

(c). The agitator in the emulsification vessel plays a vital role in providing adequate shear forces while holding the wax below the water surface.

(d). As liquid/liquid contact must occur between molten wax and water during the emulsification process, the water temperature must not be more than 15°C below the melting point of the wax. This limits the atmospheric method of wax emulsion formation to waxes having a melting point less than 110°C.

(e). The emulsification process essentially involves the disruption of the oil phase into stable sub-microscopic particles. In the case of a wax emulsion, this must be achieved more rapidly than the rate of cooling to the solid phase. This is the main difference between conventional liquid/liquid emulsification and wax emulsification.

7. - APPLICATION OF EXPERIMENTAL RESULTS TO COMMERCIAL PROCESSES

7.1. Summary of Findings.

The findings of the study may be summarised as follows:-

(a). The identification of sources of practical information on the subject of wax emulsions. These sources originated from wax suppliers.

(b). The confirmation, identification and subsequent ranking of the system variables. Key variables have been established and suggested ranges of operating values indicated for the remainder.

(c). The mechanism of wax emulsification has been investigated and energy balances applied to the wax to water process studied in this project. Good agreement has been found between theoretical energy requirements and those measured experimentally.

(d). Reliable methods of specifying and/or designing large scale wax emulsification equipment have been devised.

(e). New techniques for wax emulsification have been postulated and areas where future research might prove beneficial have been indicated.

7.2. Disadvantages of Typical Present Day Production Plant.

Before listing the disadvantages of typical production plants, it is perhaps worth repeating the main conclusions from Section 2; namely that little change in production equipment has occurred since production methods were first documented i.e. approximately sixty years ago. Traditionally, a wax emulsion plant comprises a melting pot or kettle and a second vessel containing water for emulsification. It is suspected that because few attempts have been made to research the system variables, many wax emulsions are manufactured under conditions of minimal control. Most traditional plants for surface emulsification have little instrumentation fitted to them. Consequently, the main disadvantages of typical batch wise wax emulsion making equipment may be summarised as:-

(a) The lack of process control.

That is the inability to effectively control the wax feed rate; the degree of agitation; the extent of emulsifier loss or degradation; the wax and water temperatures.

(b) Insufficient Agitation.

This is frequently so with respect to the wax feed rates that are to be emulsified.

(c) Unsatisfactory Arrangements for Wax Addition.

This is usually achieved by gravity, making feed pipe blockage a regular occurrence. Arrangements for insulating or tracing wax feed pipes are usually inadequate, such that over cooled wax is delivered for emulsification.

Drop heights (i.e. the distance the wax travels from the melt vessel to the water surface), tend to be larger than advisable which leads to over-cooled wax. Though attempts have been made to overcome the problems by subsurface wax addition through a traced pipe, they are only partly successful due to blockage. This blockage is usually caused by water backing up the feed pipe and either solidifying wax or causing a vapour lock. In addition, unless the tracing is effective, wax residues build up in such a system.

(d) A direct consequence of some of the problems described above is the build up of waxy residues in the emulsion vessel. Substandard emulsions often contain 'fragments' of unemulsified wax which accumulates on the vessel walls, the agitator blades and baffles. Such residues can frequently contaminate subsequent batches, giving them an abnormally high level of suspended wax which later creams out in the final product. The removal of such material from the product is difficult, due to its relatively small size and adhesive nature, making filtration difficult.

(e) With most currently used equipment, substandard batches are not uncommon. When this situation occurs, rework procedures are generally impractical and uneconomic, frequently leaving an effluent disposal problem.

7.3. Possibilities for Process Improvements based on Experimental Findings.

The opportunities to effect improvements may be classified into categories as follows:-

7.3.1. Improvements to formula.
7.3.2. Improvements to process design and control.
7.3.3. Opportunities for reworking substandard product.

The above possibilities will now be discussed in some detail.

7.3.1. Formula Improvements.

Studies completed in Sections 4 and 5 showed that the emulsifier levels and the degree of saponification (for those waxes that require it), have a marked influence on the finished emulsion. Later studies on the mechanism completed in Section 6, indicated that the reduction of the interfacial tension and wax solidification temperatures were further key factors controlling emulsification.

However, apart from the successful formation of a wax emulsion, the emulsifier levels were seen to be of paramount importance in three other respects. As stated by Becher (1) and Sherman (24), the type and level of emulsifier can control emulsion type, particle size and stability. The wax emulsion used for the study was formulated with a nonionic emulsifier and free alkali (potassium hydroxide). This formula is described in Section 3 and the effects of alkali on emulsion particle size demonstrated in Section 5. These effects are demonstrated for other wax emulsions also in Section 5.

To summarise, if the following guide lines are followed when formulating a wax emulsion, a satisfactory product should result.

(a). Calculate the theoretical amount of emulsifier required as shown in Section 5.7.

(b). If possible, experimentally check that the theoretical level of emulsifier reduces interfacial tension at the oil (molten wax) and water interface in the range 0.5 - 3.0 dynes/cm. This may be achieved by use of a du Nouy Tensiometer (147).

(c). Set free alkali (if required) at 10% of emulsifier level.

(d). Try laboratory manufacture using apparatus similar to that illustrated in Figure 3.1., Section 3.

(e). Apply quality assessment techniques (see Section 4) and if the result is unsatisfactory, consult Table 7.1.

TABLE 7.1. THE OPTIMISATION OF EMULSIFIER LEVELS FOR WAX EMULSIONS

Defect in Wax Emulsion	Probable Cause	Recommended Action
1. Complete phase separation on cooling.	Insufficient emulsifier	Raise emulsifier level by 10%, 25% then 50%, 100%, 200% in successive batches. Repeat level which produces good result. See also 3 below.
2. Emulsion of wrong type, e.g. oil out rather than water out.	Consult emulsifier suppliers data and determine HLB value. 3-6 → w/o 8-18 → o/w	Choose new emulsifier.
3. Emulsion not sufficiently fine. e.g. containing many particles greater than 10 microns.	a. Insufficient saponification.	a. Allow more reaction time in melt vessel.
	b. Insufficient free alkali.	b. Raise level by + 50%.
	c. Insufficient emulsifier.	c. Raise level by +10%, then +25, +50, +100%.
4. Emulsion contains much fragmented wax (See Section 6) e.g. 50 microns to several millimetres.	Wax too cold during emulsification - probably unrelated to formulae.	Check drop point of wax melt is less than 110°C. If not, pressure methods may be necessary.
5. Emulsion very large macroscopic particles often several centimetres in size.	Insufficient emulsifiable wax in wax melt.	Investigate alternative wax blends.

7.3.2. Process Improvements.

(a). Good control of temperatures can help considerably in preventing substandard wax emulsions. Although wax melt temperatures are generally controlled, water temperatures seem to be more of a problem. Perhaps this is because most plants have the capacity to overheat and boil water whereas wax can only be overheated. A second reason is that the water tends to be metered to the emulsion vessel, the heating cycle started and then it is left unattended, attention being turned to wax preparation. Both events are strong reasons for greater control, that is the provision of suitable instrumentation. Boiling water during emulsification is almost as disadvantageous as water which is too cold. This is because it contains bubbles of vapour thereby causing a third interface i.e. water/vapour/wax. Heavy fragmentation of wax is usually the result, leading to a substandard emulsion.

An ideal temperature for many waxes is 95^{o}C as this allows sufficient flexibility for likely plant fluctuations (e.g. $\pm$ 4^{o}C). However, lower temperatures may be used with low melting wax blends. It is usual to aim for a 10 - 15^{o}C (maximum) temperature difference between wax and water, the wax usually being the higher. Nevertheless, from a quality viewpoint, there is no reason why the temperatures cannot be equal or the water temperature the highest. If, as is usually the case, the water temperature is the lowest and the differential widens, the wax will tend to solidify before it has been emulsified. An emulsion containing a high proportion of 'fragments' will result. Therefore the guidelines on temperatures are:-

Wax Drop Point less than 100°C - Water at 95°C - surface addition.

Wax Drop Point greater than 100°C but less than 110°C - Water at 95°C - Surface addition.

Wax Drop Point greater than 110°C - Pressure emulsification methods are necessary.

Note that to a limited extent, the drop point may often be depressed by the use of extra emulsifier.

(b). Effective control of the wax melt feed rate during emulsification is most important. The consequence of overloading the agitation system are discussed in Section 5.6.6. Unfortunately this situation is a frequent occurrence with much industrial plant. In many cases, the equipment has not been designed but assembled together in the hope that it will suffice for emulsion manufacture. Often the agitation system cannot cope with the full wax feed rate possible from the melt vessel and pipework. The problem is usually compounded by inadequate steam or heat tracing and the fact that many process operators fully open feed valves to avoid possible blockage and to decrease batch time. On the other hand, a wax feed rate may be initially low due to partially obstructed pipework. This may change rapidly and independently of the feed valve setting, as the residual wax melts and allows full bore flow again.

The remedies are as follows:-

(i). The calculation of the optimum feed rate for the agitation system using the methods of Section 5.6.

(ii). Pumped wax feed incorporating an efficient heat tracing system for pump, valves and pipework. This will minimise the risk of blockage during emulsification and reduce wax hold up in the pipework.

(iii). Alternatively if either of the above are impractical or impossible, the provision of the optimum feed rate for the given agitation system by fixing the feed valve setting at this rate. As long as the heat tracing system is efficient, blockage should be reduced to a minimum and, though batches may take somewhat longer, it should not be possible to over-load the system.

(c). The degree of agitation in the emulsion vessel is a very important factor in the actual 'formation' of the emulsion. Design guidelines have been formulated during the study whereby the accent is placed in two areas:-

(i). In order to provide sufficient downthrust to submerge the required wax feed rate.

(ii). In order to apply sufficient shear force to effect droplet formation before the phase change occurs.

As shown in Section 5.5.12, consideration (i) above tends to be the overbearing one as (ii) normally follows as a consequence. Apart from these considerations, agitation may be by any convenient impellor system e.g. marine propellors, turbines or pitched paddles, remembering that downthrust is a major requirement for surface addition methods. Further, it does not appear to be mandatory to create conditions of efficient mixing, though such conditions (e.g. turbulence), are often adequate for wax emulsification.

(d). Maintenance of Control of Conditions in the Wax Melt Vessel.

The creation of satisfactory conditions in the wax melt vessel can greatly increase the chance of a successful product. Melt temperatures have already been discussed in (a) above but agitation is important also. This is particularly pertinent where the wax must be saponified prior to emulsification. The saponification reaction is quite rapid at temperatures normally encountered with wax melts. As shown in Section 5.5.7 , it can be complete in two to five minutes, but only under good mixing conditions. Usually potassium hydroxide solution is used (50% w/w), and the addition initiates the violent evolution of water vapour. Water is also a reaction by-product and good agitation (usually 15 minutes is allowed commercially), facilitates its removal as vapour and appears to increase reaction rate. However, the agitator used must also be powerful as the saponification is usually completed with the emulsifier present and, prior to water removal, an oil out emulsion forms. At this point, the wax melt viscosity tends to a maximum value. It is then necessary to effect water removal to destroy the emulsion and return the melt viscosity to normal levels. Agitation is the means to effect this change without undue delay.

After saponification, (if required), good mixing of the wax melt is important to ensure distribution of the emulsifier and heat transfer to the wax. A further consideration is relevant when utilising anionic emulsifiers such as amine soaps. These materials are usually degraded or volatilised at wax melt temperatures and are formed 'in situ' prior to emulsification. Long holding periods are disadvantageous and good mixing enables these reagents to be added to the melt a few minutes before the emulsion is formed. The problem is much reduced with the nonionic emulsifiers.

Referring again to anionic systems, it is often preferable to have a closed melt vessel in order to minimise losses of the volatile amines. Some plants have a second vessel for this purpose, that is a vessel for melting and a sealable vessel for adding emulsifiers prior to emulsification. As shown in Section 5.5.9., this is an unnecessary consideration for nonionic emulsifiers.

7.3.3. Opportunities for Reworking Substandard Emulsions.

(a). Introduction.

In terms of correcting substandard emulsions, there are two basic categories. Those containing waxes which may be liquified at temperatures below 100°C and those which cannot. The former type may usually be reworked by reheating and mechanical homogenisation techniques. In this case, the wax is first liquified then re-dispersed by a rotary, pressure or ultrasonic homogeniser. These devices are described by Becher (1) and though the method is largely fool-proof, it is sometimes necessary to correct the initial fault or deficiencies, prior to reworking.

The wax emulsions containing waxes which melt in excess of 100°C pose a problem with the type of equipment investigated in this study. They cannot be liquified and hence redispersed. There are however, possibilities to re-filter the substandard emulsion or otherwise separate off wax fragments, (if these are the sole reasons for rejection); but there are practical difficulties. Wax emulsions are notoriously difficult to filter on account of the fine particulates that they contain and because of their adhesive nature. Further, if attempting such an operation, one must ensure that the resulting filtrate is both stable and of sufficient concentration for the purpose intended.

A further possibility for the recovery of waxes melting greater than 100°C is to completely break the emulsion by raising the temperature and subjecting it to an extreme of pH.

The waxy layer would then be separated, remelted and re-emulsified, while the aqueous layer could be neutralised and discarded. The method can be shown to be uneconomic and is not recommended.

Pressure is therefore needed to reliquify such a wax blend in its aqueous medium, and there are claims that pressure emulsification equipment is ideally suited to this purpose (84). The process of pressure emulsification has already been described in Sections 2 and 6, and although only preliminary work has been attempted in this study, it would seem that the manufacturer who has made the somewhat greater investment in pressure equipment has a distinct advantage here. Pressure emulsification is therefore the third and best way to rework emulsions containing waxes with melting points greater than 100°C. However, rework procedures are practically effected for high melting wax blends, a review of typical emulsion defects is helpful.

(b). Typical Wax Emulsion Defects as Characterised by Type of Wax Particles in Emulsion.

Most water out wax emulsions consist of four types of particles and these are summarised in Table 7.2. Wax emulsions of the oil out variety seldom require reworking and always involve low melting waxes. They have therefore been excluded from this discussion.

TABLE 7.2.

WAX EMULSION PARTICLES

Type	Shape	Size	Numbers	Origin
1. True droplets.	Spherical.	Usually very small sub-microscopic.	Very large. These form the bulk of wax in the emulsion.	Disruption of the molten wax during emulsification.
2. Aggregates.	Clusters of true droplets.	Microscopic.	Usually small.	Aggregation due to partial failure of protective film.
3. Coalesced drops.	Spherical or polyhedral.	Microscopic.	Usually small. Sometimes large if emulsion very unstable.	Coalesced type 1 or 2 particles.
4. Fragments.	Irregular.	Microscopic and Macroscopic.	Often large.	These are particles of unemulsified wax originated from wax which solidifies prior to droplet formation (emulsification).

A substandard wax emulsion usually contains a high proportion of type 4 particles and sometimes type 2 and 3 particles. In fact, by examining the substandard emulsion under the microscope, a diagnosis of the cause is frequently possible. For example;

- a high proportion of type 4 particles usually indicates that either emulsification temperatures were too low; that insufficient shear (or agitation) was applied during emulsification or that the wax blend requires pressure emulsification. These are illustrated in plate 7.1.
- a large number of type 2 and/or 3 particles indicates that there are problems with the emulsifier system i.e. either insufficient has been used, that is,it is badly distributed or that it is unsuitable. These are illustrated in plate 7.2. A satisfactory emulsion is illustrated in plate 7.3.

(c). Recommended Rework Procedure.

Before attempting the rework of any wax emulsion, it is preferable to know the type of emulsion and why it has failed. A preliminary microscopic examination is recommended for this purpose. The emulsion may then be reworked as follows:-

(i). Correct initial deficiency e.g. add extra emulsifier; free alkali or waxes (see Table 7.1.).

(ii). Place the emulsion in a pressure vessel equipped with powerful agitator/homogeniser and a heating capability.

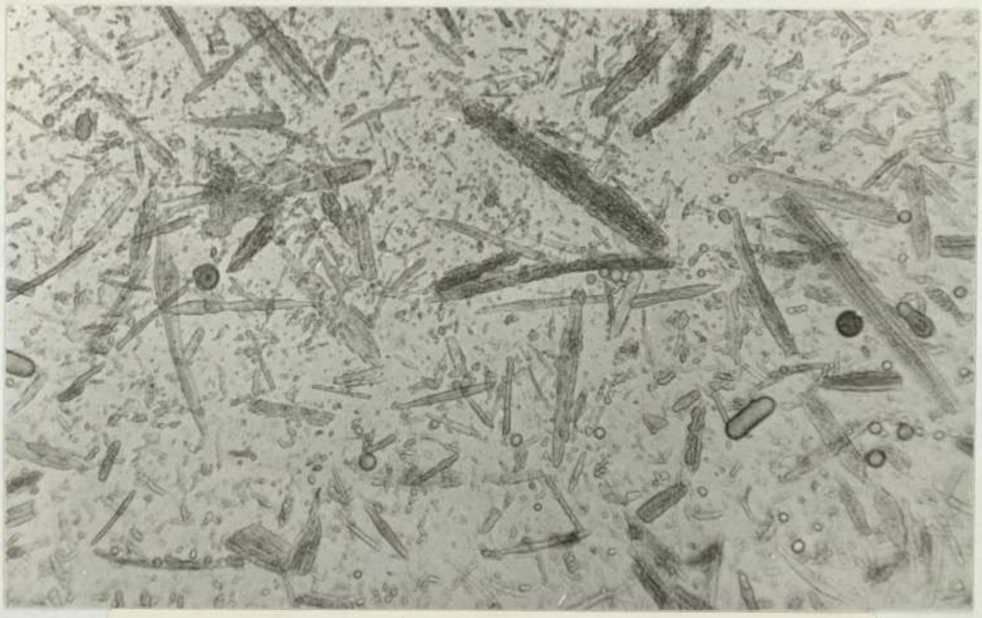


PLATE 7.1.

Type 4 Wax Particles (fragments)

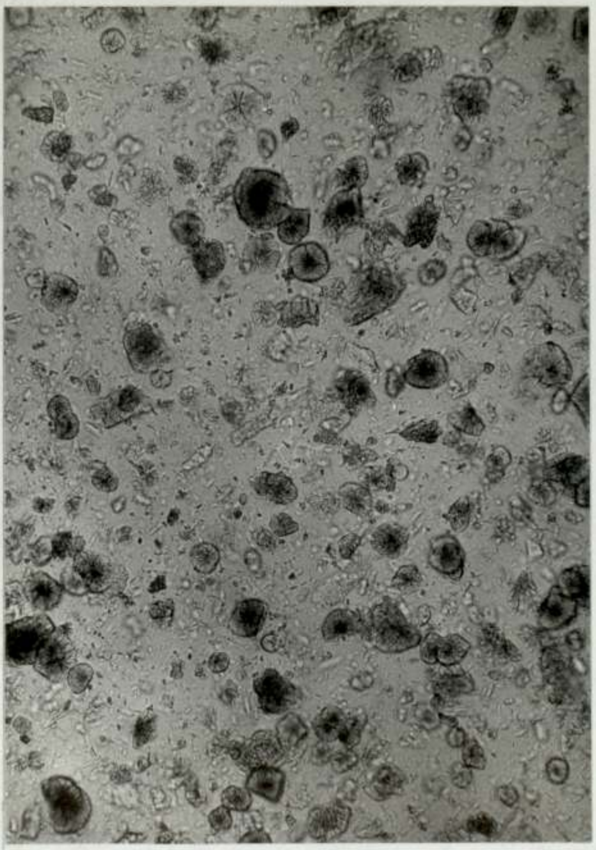


PLATE 7.2.

Type 2 and 3 Wax Particles (agglomerates)

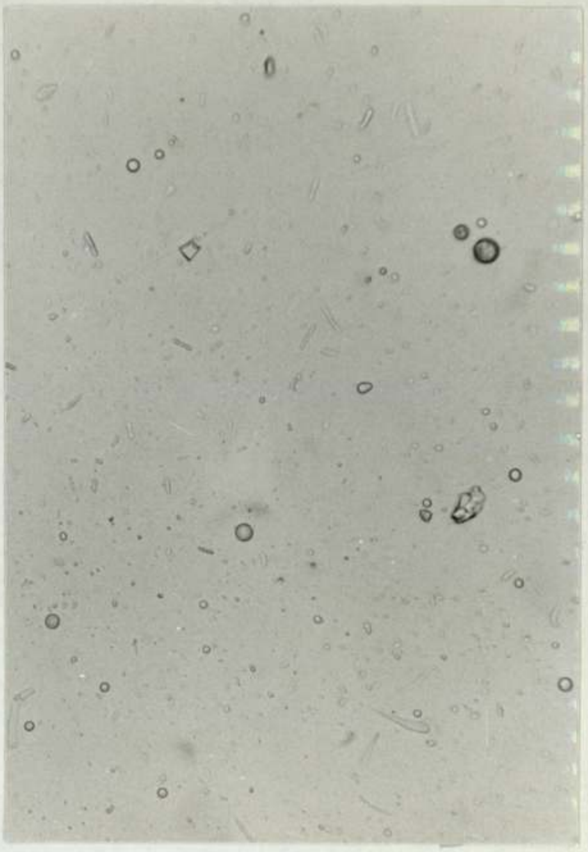


PLATE 7.3.

Good Wax Emulsion (spherical particles)

Typically the type of equipment for pressure emulsification (described in Section 2) would be used.

(iii). Raise the temperature (and pressure) to at least $5^{0}C$ above the wax blend drop point and, applying maximum agitation, hold in this condition for 10 - 15 minutes.

(iv). Rapidly cool to ambient temperatures (using heat exchange).

The above method should produce an acceptable emulsion, i.e. one which has suitably small particle size and good stability. It may not produce equivalent particle size to a correctly manufactured emulsion however, and in such a case will tend to be more opaque. It is possible that such difficulties may be overcome by future work (See Section 9).

8. - OVERALL CONCLUSIONS

8.1. State of the Art.

The following conclusions were drawn from a review of the literature, a knowledge of industrial practice and from the difficulties encountered in obtaining information during the study:-

(a). The manufacture of wax emulsions has received little attention over the last 60 years.

(b). The bulk of the information that is available (concerning formulae and preparative methods), originates from the wax suppliers. Some data has been published by manufacturers.

(c). The literature does not compare or contrast the different wax emulsion formulations nor high light problems areas.

(d). The available literature does not consider methods of quality control for wax emulsions.

(e). No detailed description of the manufacturing techniques and how and where to apply them is given in the literature.

(f). The reworking of substandard emulsions is mentioned in some wax suppliers data but very few details on technique are published.

(g). No description, discussion or other published information is available dealing with the mechanism by which wax emulsions form. Most information sources appear to group wax emulsions with conventional liquid/liquid types and assume similar mechanisms apply.

8.2. Quality Control.

Wax emulsion quality may be judged by the two criteria of appearance and performance.

The most useful method of appearance is by the gravimetric determination of the percentage of particles greater than 10 micron (See Section 4.4.4.) If the disperse phase is deformable and therefore capable of passing through a filter, microscopic examination can be employed. These methods can be both qualitative and quantitative.

Other useful qualitative tests include light transmission (See Section 4.4.2.and degree of phase separation (See Section 4.1.).

Performance criteria are more difficult to apply from a quality control standpoint. The study concludes that the assessment of stability is the most reliable measure of wax emulsion performance and that this in turn is best measured by the freeze/thaw method detailed in Section 4.

8.3. System Variables.

(a). Fourteen variables have been identified and investigated.

Only four of these are critical namely, emulsifier and free alkali levels which constitute the emulsifier system and rate of wax addition and degree of agitation which control droplet formation.

(b). Wax emulsification by surface addition involves a phase change, the critical temperature parameter is the differential between the wax drop point and the water temperature. It is concluded that for surface methods, this value must not exceed 15^{o}C.

8.4. Mechanism of Formation.

The conclusions from the study were as follows:-

(a). The emulsification of wax proceeds in a manner similar to other conventional emulsions i.e. by liquid liquid contact.

(b). With the emulsification of wax, at least one additional difficulty exists, namely the formation of droplets before the wax solidifies.

(c). Considering the particular method under study (i.e. atmospheric surface addition), the process proceeds via the erosion of wax filaments formed by pouring the molten wax stream onto the water surface.

(d). Wax filament erosion occurs by the application of shear forces which disrupt the wax/water interface. These forces are in turn induced by differential velocities between wax and water.

8.5. Reworking Substandard Wax Emulsions.

(a). Substandard wax emulsions containing wax that may be liquified at temperatures below 100°C can be reworked by reheating and mechanical break-up of the wax particles (homogenisation).

(b). Substandard wax emulsions containing wax that cannot be liquified below 100°C cannot be reworked using the equipment studied in this project. Pressure emulsification equipment is required.

(c). When wax emulsions are reworked by pressure emulsification methods, it is generally impossible to match the quality (in terms of particle size), with that of a correctly made batch. Substantial improvements are however possible especially if the initial fault is determined (e.g. insufficient emulsifier) and corrected during reprocessing.

8.6. Applications to Commercial Processes.

(a). Wax emulsions containing wax blends with melting points less than 100°C may be conveniently processed by surface addition methods conducted at atmospheric pressure. However, for those wax emulsions containing solvent, silicones and perfumes, further (mechanical) particle size reduction is frequently necessary via a homogeniser.

(b). Wax blends with melting points of up to 110°C can usually be successfully emulsified by atmospheric surface methods without additional homogenisation. Pressure emulsification may also be used.

(c). When melting points of wax blends exceed 110°C, pressure emulsification apparatus is mandatory due to the fact that in such cases, the wax solidifies before droplet formation can fully occur.

9. - FUTURE WORK

9.1. Reprocessing of Substandard Wax Emulsions.

An area that warrants future work is the recycling or reprocessing of substandard wax emulsions containing waxes non-liquifiable below the boiling point of water. As reported in Sections 2 and 8, some degree of success has been achieved via the use of pressure emulsification equipment. However, the process does not appear to be capable of producing quality equivalent to fresh material. Further research could prove beneficial.

9.2. Measurement of Emulsion Stability.

The measurement of emulsion stabilities in general could be improved by further study. Most of the reported activity has been with somewhat idealised systems known to possess diminished stability. Recent investigations by Sherman (148)(149) involving the measurement of phase inversion temperatures as a means of stability assessment, may perhaps be developed for commercial emulsions. On the other hand, because of the numerous ingredients, e.g. waxes, oils, perfumes, in such products, phase inversion phenomena could be less precise than with the somewhat idealised systems studied to date.

The techniques used in this study are designed to measure the liklihood of creaming and assess the efficiency of the emulsifier in preventing aggregation, coalescence or inversion. However, although it is anticipated that these tests will be suitable for the industrial quality control laboratory and find wide usage, they will not be universally applicable. For example, some emulsions will not be effected in a readily measureable way by varying pH or freeze/thaw cycles. Such an emulsion might respond to electrical potential and this might be used as a quality parameter. By further research in this area, it may be possible to devise a series of tests that will enable the stability of all emulsions to be measured and referred to a datum in a similar fashion to the use of the hydrophile/lipophile balance.

9.3. Pressure Emulsification.

This study has concentrated on atmospheric surface methods for the emulsification of wax. These methods date back to the time when production techniques were first documented and although this investigation has produced various improvements, it is concluded that future work should be directed toward pressure emulsification. The rationale for this conclusion is based on the following observations.

(a). Many wax emulsions containing waxes liquifiable below the boiling point of water, (at 1 atmosphere), may be produced (and when necessary reworked), in a satisfactory manner by surface addition methods. This leaves little scope for significant improvements in either equipment or technique for this type of emulsion.

(b). When the waxes to be emulsified melt in the range 100-110°C, they may be processed conveniently by atmospheric surface addition methods provided the recommendations outlined in Sections 5 and 7 are followed. In addition, substandard batches may be reworked via pressure emulsification equipment, also described in Section 7.

(c). Wax blends which have higher melting ranges than (a) and (b) above, i.e. greater than 110°C, can only be handled by pressure emulsification equipment.

(d). Consumer requirements for polishes which form a hard tough gloss film has induced manufacturers to use higher melting polyethylene waxes. This trend continues (150).

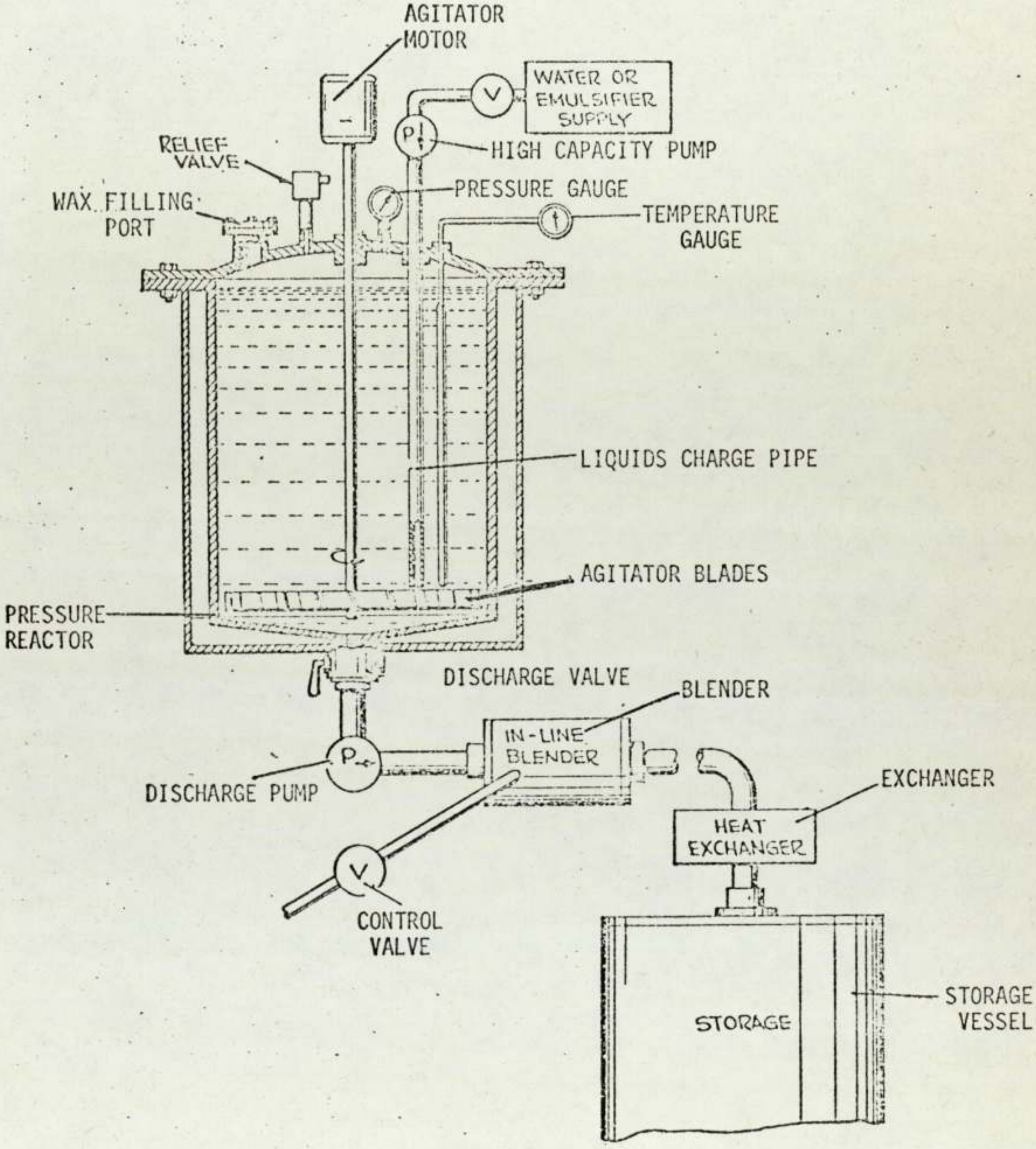
Therefore pressure emulsification appears to be suitable for at least two categories of waxes used to make emulsions and it seems to provide a possibility to recover substandard product. However, as already discussed in Section 8, the process is far from perfect and the equipment normally utilised has many disadvantages. These will now be reviewed in order to highlight possible areas for future development.

9.3.1. Disadvantages of Current Pressure Emulsification Methods.

Most plants for the emulsification of wax under pressure consist of a pressure vessel equipped with a powerful agitator and a high throughput pump to charge water to the pressure vessel. A typical arrangement is shown in Figure 9.1. and normal working conditions are 25 - 40 psig and 110 - 135°C. The disadvantages of such a system, mostly compared with

FIGURE 9.1.

TYPICAL PRESSURE EMULSIFICATION SYSTEM



conventional surface addition plant are listed below:-

(a). Comparatively high capital cost - shown in Table 9.1. - which compares a surface wax emulsion plant of batch size of 2 tons with a pressure plant of the same size.

(b). High power consumption from the agitator. Most wax melts are very viscous, and it is normally necessary to go through an oil out stage during which extremely high viscosities are encountered.

(c). The process is still batchwise with a batch time of approximately 1 - 1½ hours. Although this compares favourably with the older steam kettle type of surface addition plant, it is about the same as modern surface plant. The major part of the processing time in each case is used to bring the wax to process temperature.

(d). The need to operate with a relatively large pressure vessel incorporating all the mandatory safety procedures. Although this may seem a minimal disadvantage, it causes concern to many manufacturers who have no experience of pressure work.

(e). The need to have a separate water heating system. As described in Section 2 and Appendix I, the process involves the high speed injection of hot water to the pressure vessel.

TABLE 9.1. - COMPARISON OF PRESSURE AND ATMOSPHERIC EMULSIFICATION PLANT

ATMOSPHERIC PLANT		PRESSURE PLANT	
ITEMS	COSTS £	ITEMS	COSTS £
Wax Conveyor	600	Wax Conveyor	600
High Speed Wax Melter	8000		
Saponification vessel (1600 litre)	3500		
Agitator for saponification vessel	1500		
Jacketed Emulsion vessel (4000 litre)	10000	Jacketed Pressure Emulsion vessel (2500 litre)*	5400
Varispeed agitator for above	2000	Varispeed agitator for above	2000
		Jacketed hot water vessel (1000 litre)	4200
Heat Exchanger (cooler)	4000	Heat Exchanger (cooler)	3000
Pumps (2)	800	Water Feed Pump	1500
Pipe and Valves	3000	Pipe and Valves	1000
Insulation	1000	Insulation	500
Controls and instruments	1200	Controls and instruments	1000
Total basic capital cost	£35600	Total basic capital cost	£19200
i.e. excluding drawing/design changes; steelwork, electrics and civils		i.e. excluding drawing/design changes; steelwork, electrics and civils	

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*Vessel smaller because emulsion made at higher concentration than diluted.

Estimate for inline plant is £16 - £20,000 occupying approximately 1/10th of floor area of atmospheric plant.

9.3.2. Areas of Future Investigation.

A more convenient form of pressure working is via pipe lines which are not subject to the same safety constraints e.g. inspection by outside agencies, and are generally well within the experience and capability of most manufacturers. From the conclusions in Section 6 on mechanism of formation, it would seem that the disruption of the wax/water interface could be achieved by any convenient device capable of applying shear forces to it. Therefore, inline blending should be capable of yielding good quality wax emulsions either continuously or batchwise. A proposed arrangement for the production of wax emulsions by a pressure inline blending is illustrated in Figure 9.2. Referring to this diagram, waxes would be charged to the high speed (tubular) melter, and when melted, emulsifier(s) and if used, alkali added to complete the melt. This would then be transferred by gravity to the wax reservoir which would be a heated and closed vessel where the melt may be held at emulsification temperatures. Metering pumps (P1 and P2) would deliver the correct proportions of wax and hot water (also supplied to P2 at the emulsification temperature), to the hot blender to give as concentrated an emulsion as possible.

Following passage through the hot blender, a third metering pump would deliver the balance of cold water to complete the emulsion and also to cool it. Care would be required in setting the water balance in order to avoid the formation of a viscous emulsion which would be difficult to

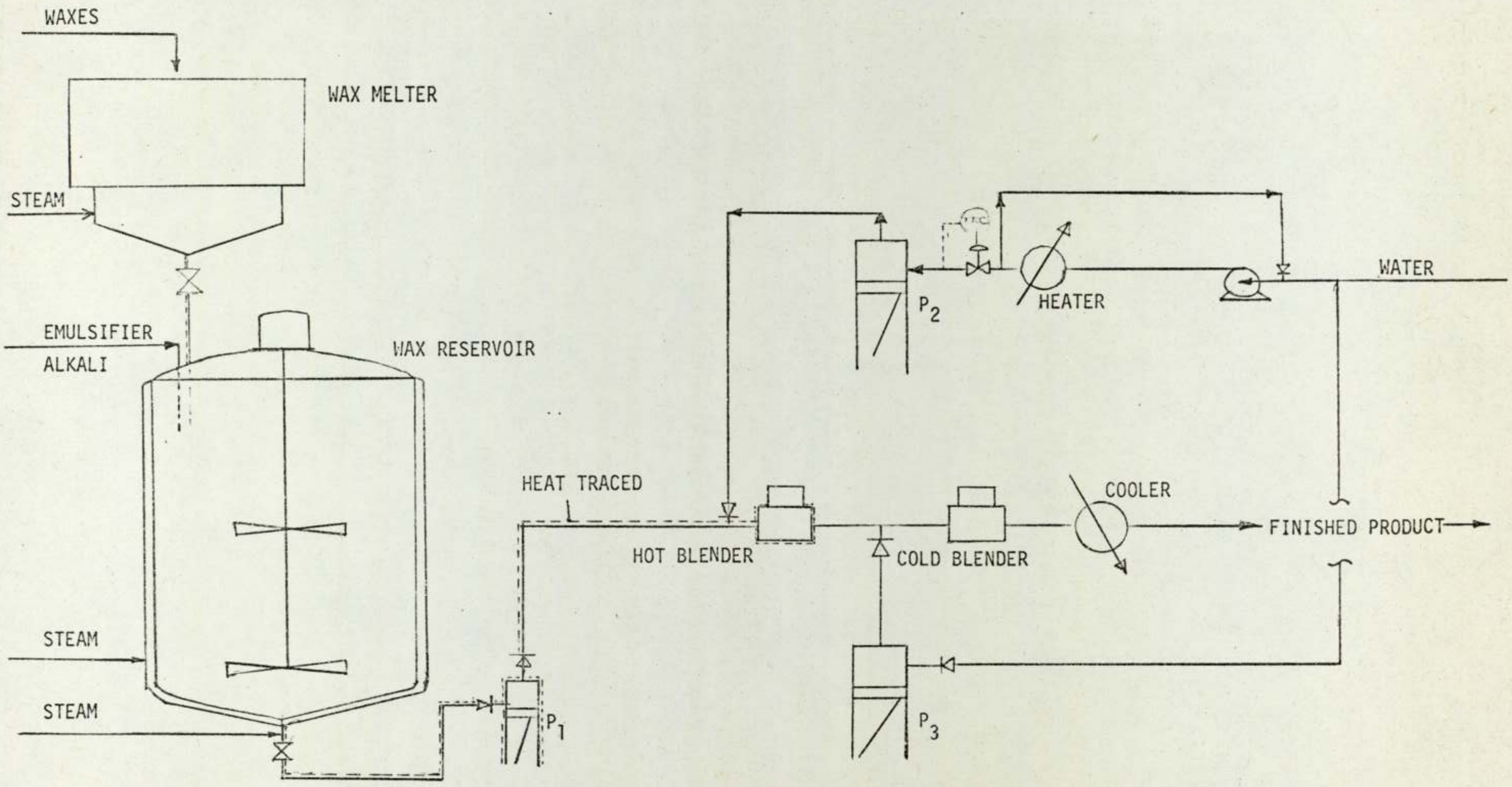

FIGURE 9.2. - PROPOSED ARRANGEMENTS FOR PRESSURE EMULSIFICATION

handle in this type of equipment. A second (cold) blender would ensure homogeniety and a cooler would deliver the finished emulsion at near ambient temperatures.

Such a plant would occupy minimal floor space estimated at 1/10 of space required by conventional surface plant and would be capable of batch, continuous or intermittent operation. When on continuous mode, the reservoir would feed the metering and blending equipment while a second 'batch' of wax melt was prepared then transferred.

Intermittent operation could be achieved by simply stopping the wax feed, then diverting the small quantity of residual emulsion produced (by clearing the system), to waste. As the pumps P1 and P2 would be designed to give a constant ratio of wax/water and the pump P3 similarly designed to ratio the dilution water to the concentrated emulsion, the production cycle could be continued by simply restarting all the pumps via a master switch.

Varied wax blends would easily be possible with this equipment and it should be capable of making virtually any wax emulsion likely to be required. With the high solvent containing types, it may be necessary to interpose a mechanical homogenisation step prior to cooling. In fact, the system could have many advantages without the disadvantages associated with either of the present methods. Therefore it is recommended that further work be attempted toward such a process.

An extension of the above is the direct processing of solid wax by inline pressure techniques. That is, the production of a premix slurry of solid wax beads, alkali and hot water. Waxes normally supplied in slab form e.g. Beeswax and other natural waxes, would require pelletising. This premix would be fed into the pressure/heating circuit via an eccentric screw or 'Mono' pump (P1). (See Figure 9.3). Once the slurry had passed through the pump its pressure would be above atmospheric for example 25 psig. It would then pass to the heating circuit via pump P2 and be recycled around the circuit (operating at pump pressure e.g. 25 psig), until all the wax melted and the resultant 2 phases were raised to emulsification temperature. A temperature recorder/controller would monitor the outlet flow from the heating circuit via valve V_2, when it would pass to the homogenisation circuit. Before entering this circuit, a metering pump P3 would inject the appropriate quantity of emulsifier(s), in ratio with the flow.

In the homogenisation circuit, actual emulsification of wax would occur, the particles being reduced in size by the inline homogeniser. Finally, the product from the homogeniser circuit would be diluted by further water injection (via metering pump P4), and an inline blender would ensure homogeneity prior to cooling and storage. The above system is illustrated in Figure 9.3. and a test apparatus actually assembled to verify the principles involved, in Figure 9.4. This latter diagram illustrates equipment which has actually been used to make emulsions by inline pressure emulsification.

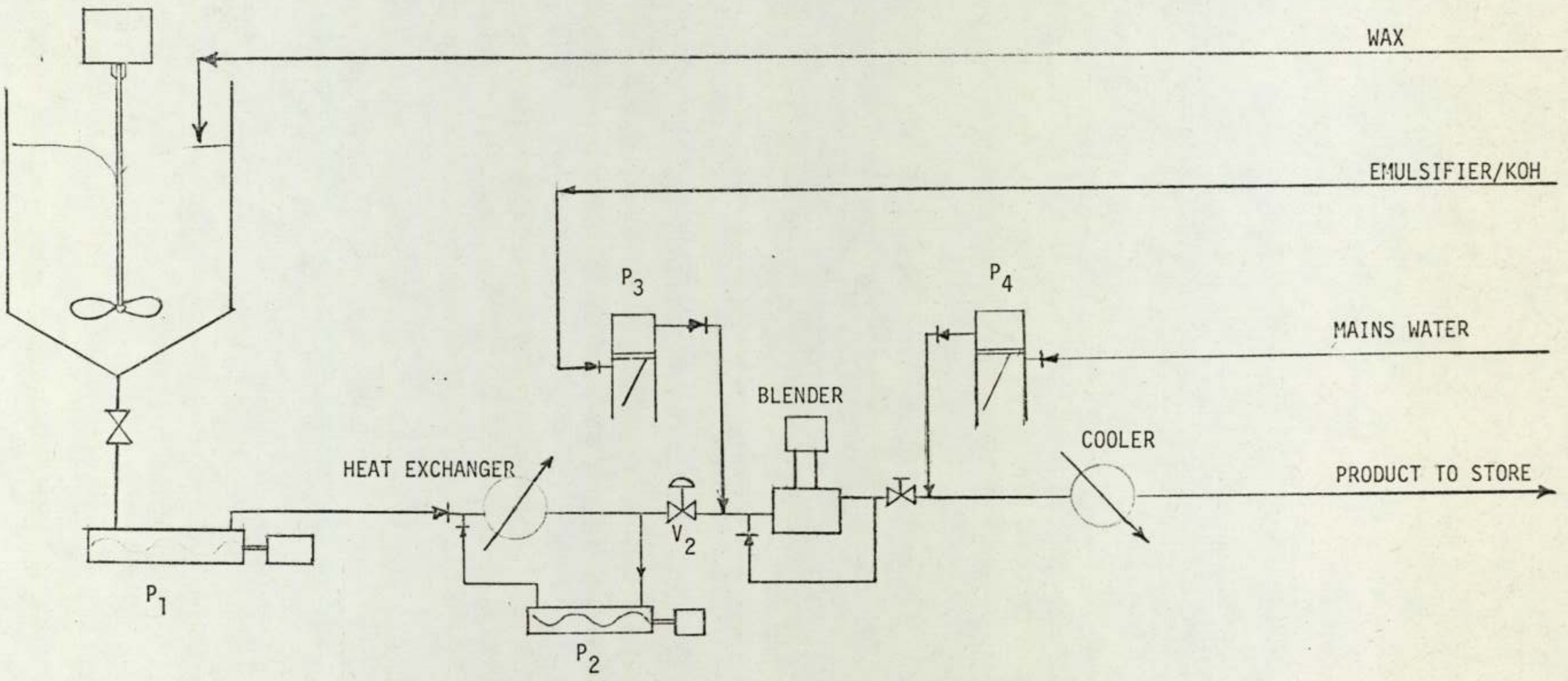

FIGURE 9.3. - PRESSURE EMULSIFICATION USING INLINE BLENDING (SOLID FEED)

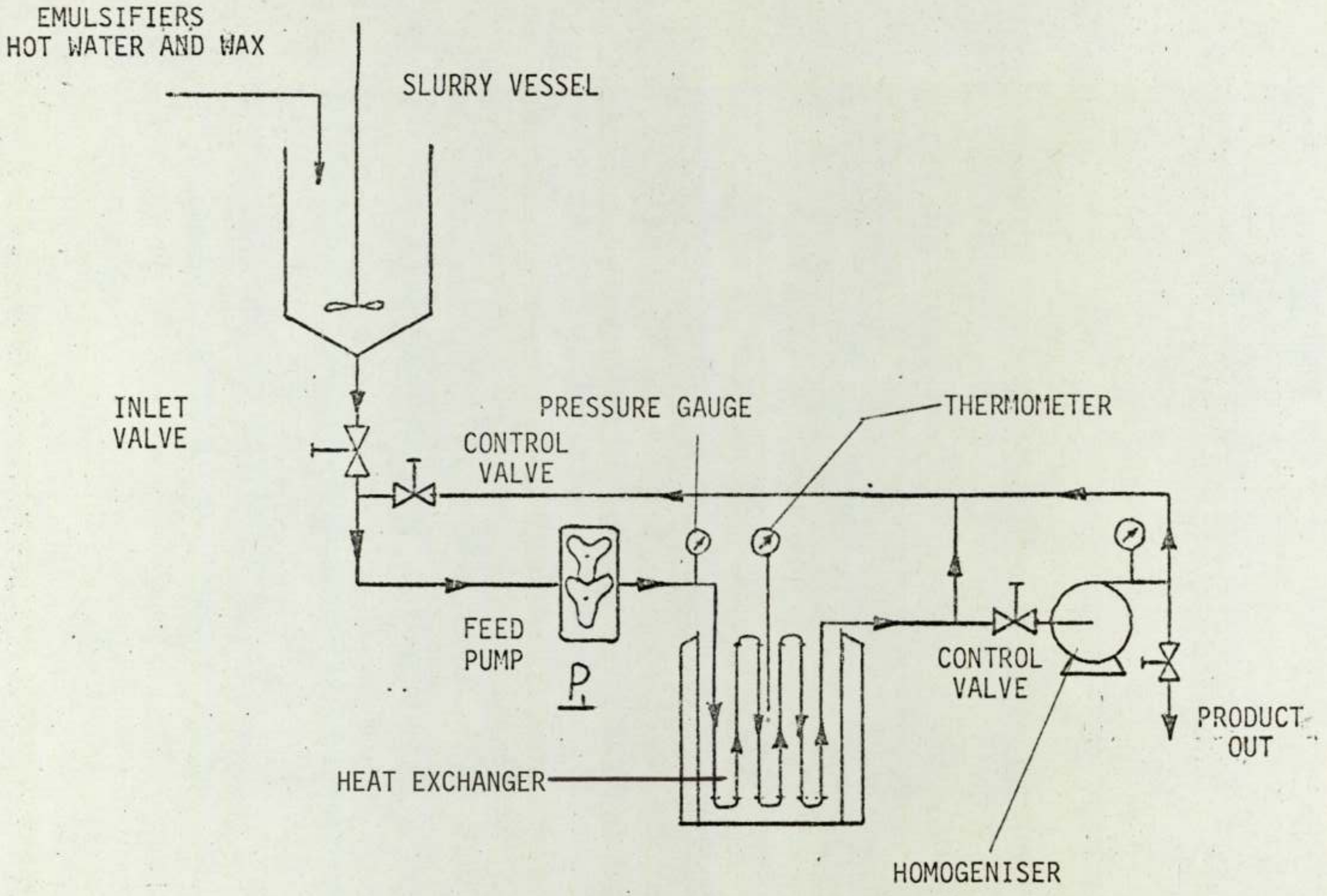

FIGURE 9.4.

PRESSURE EMULSIFICATION BY INLINE BLENDING -

APPARATUS OF VERIFICATION OF PRINCIPLES

It may be the subject of further study by Johnson Wax and a provisional patent has been applied for.

SECTION 10. - REFERENCES.

(1). Becher, P., 1966, "Emulsions: Theory and Practice", 2nd edition, Reinhold, New York.

(2). Levius, H.P. and Drummond, F.G., 1953, J. Pharm., Pharmacol, 10, 743 - 756.

(3). Levy, G.B., 1955, "Accelerated Shelf Testing", Drug and Cosmetic Industry, 76, (4), 472 - 473.

(4). American Society for Testing Materials, 1970, Method D1796, 66.

(5). Kroner, A.A., 1949, Soap and Sanitary Chem., 10, 137 - 145.

(6). Appino, J.B., Christian, J.E., and Banker, G.S., 1970, J.Pharm., Sci., 59, (9), 1360 - 1362.

(7). Walker, H.W., 1947, J.Phys., and Colloid Chem., 51, 451.

(8). Fletcher, A.C., and Mayne, J.E.O., 1955, Paint Manufacture, 25, 116.

(9). Young, P.A., 1934, Pl., Physiol, 9, 795.

(10). Kistler, S.S., 1936, J. Amer. Chem. Soc., 58, 901.

(11). Cole, L.J.N., et. al., 1959, Can. J. Biochem., Physiol., 37, 821.

(12). Pospelova, K.A., et al., 1962, Colloid J., (U.S.S.R.), 24, 511.

(13). Singleton, W.S., et al., 1960, J. Amer. Oil. Chem. Assoc., 37, 88.

(14). Sherman, P., 1966, J. Food Sci., 31, 699.

(15). Merrill, R.C., 1943, Ind.Engng.Chem., Analyt.Ed., 15, 743.

(16). Garnett, E.R., 1962, J.Pharm.Sci., 51, (1), 35 - 42.

(17). Vold, R.D., and Groot, R.C., 1962, J. Phys. Chem., 65.

(18). Idem, 1963, J. Soc. Cosmetic Chem., 14, 233.

(19). Idem, 1964, J. Colloid Sci, 19, 384.

(20). Idem, 1964, J. Phys. Chem., 68, 3477.

(21). Refeld, S.J., 1962, J. Phys. Chem., 66.

(22). Fann Instrument Corporation, Tech. Bulletin, "Fann Emulsion Tester", P. O. Box 6101, 3202 Argonne St., Houston, Texas.

(23). S.C.Johnson, 1967, "Analytical Methods Manual",Racine, Wisconsin.

(24). Sherman, P., (Ed), 1969, "Emulsion Science", Academic Press, London.

(25). Overbeek, J. et al., 1950, "Advances in Colloid Science", 3, 97 - 135, Interscience Publishers Inc., N.York.

(26). Kaye, R.C. and Seager, H., 1966, Instr. Practice, Sept., 733 - 738.

(27). Coulter Electronics Ltd., 1974, "Coulter Counter Industrial Bibliography".

(28). Higuchi, W.I., et al., 1962, J. Pharm. Sci., 51, 683 - 687.

(29). Idem, 1964, J. Pharm. Sci., 53, 405 - 408.

(30). Schrenzel, M., 1966, Pharm. Acta. Helv., 41, 218 - 227.

(31). Mathews, B.A., and Rhodes, C.T., 1970, J. Colloid Sci., 32, 332.

(32). Parsons, L.W., 1922, J. Ind. Eng. Chem., 14, 787 -788.

(33). Macklay, W.N., and Ginder, E.J., 1963, J. Colloid Sci., 18, 343.

(34). Endler, F. and Gebauer, E.M., 1956, Optik, 13, 97.

(35). Becher, P. 1964, J. Colloid Sci., 19, 468.

(36). Dixon,W.J., and Massey, F.J., 1957, "Introduction to Statistical Analysis", 2nd. Edition, 292, McGraw-Hill, N.York.

(37). Shepherd, I., 1972, "Electromicrographic Studies on Furniture Care Emulsions", - internal company report.

(38). Walstra, P., 1965, Br. J. Appl. Phys., 16, 1187.

(39). Idem, 1965, Spectrovision, 13, 7.

(40). Goulden, J.D.S., and Phipps, L.W., 1960, Proc. 3rd Intern. Congr. Surface Activity, 3, 190.

(41). Goulden, J.D.S., and Sherman, P., 1962, J.Dairy Res., 29, 47.

(42). Billmeyer, F.W., 1954, J. Amer.Chem.Soc., 76, 4636.

(43). Dezelic, Gj., 1961, Croatica Chem. Acta., 33, 51.

(44). Slonim, I.Ya., 1960, Optika i Spectroskopiya, 8, 98.

(45). Langlois, G.E., et al., 1954, Rev. Sci. Instr., 25, 360.

(46). Queen, L.D. et al., March 1964, Soap and Chem. Specialities, 99 - 106.

(47). Internal Company report Anon., 1962, entitled "Use of Light Transmission for the analysis of emulsions".

(48). Lord Rayleigh , 1871, Phil. Mag., 41, 107, 274, 447.

Idem, ibid, 1897, 44, 28.

Idem, ibid, 1899, 48, 375.

(49). Van der Waarden, M., 1954, T. Colloid Sci., 9, 215.

(50). Wallach, M.L., et al.,1961, J. Chem. Phys., 34, 1796.

(51). Gledhill, R.J., 1962, J. Phys. Chem., 66, 458.

(52). Wales, M., 1962, J. Phys. Chem., 66, 1768.

(53). Dettmar, H.K., et al., 1963, Kolloid - Z, 188, 28.

(54). Weber, H.H., 1963, Kolloid - Z., 188, 40.

(55). Kerker, M., 1970, Amer. Perfumer., Cosmet., 85, (4), 43 - 51.

(56). Labrum, J.H., 1975, "Size and Velocity , techniques of high speed microscopic particles", paper delivered at "Electro-Optics 1975", Conf. Anaheim, California.

(57). Hotham, G.A., 1974, "Sizing Aerosols in real time by Pulsing Laser machine", paper presented at Aerosol measurement seminar organised by F.D.A. and Nat. Bureau of standards.

(58). Voss, K., 1976, "Particle size analysis by Laser Holography", Internal S.C.J. report.

(59). Kraemer, E.O., and Stamm, A.T., 1924, J. Amer.Chem.Soc., 46, 2709.

(60). Nicholls, J.B., et al., 1949,"Techniques of Organic Chemistry", 2nd Ed., 1, (1), 333 - 334, Interscience Publishers Inc., N.York.

(61). Whitby, K.T., 1955, J. Air Pollution Control Assoc., 5, 120.

(62). Allen, T. 1975, "Particle Size Measurement", Chapman and Hall, London.

(63). Lien, T.R. and Phillips, C.R., 1974, Environ, Sci. Technol., 8, (16), 558 - 61.

(64). Singleton, W.S., and Brown, M.L., 1965, J. Am. Oil Chemists Assoc., 42, 312 - 314.

(65). Groves, M.J., 1968, Proc. Soc. Anal. Chem., 5, 166 - 7.

(66). Sprow, F.B., 1967, A.I.Ch.E.J., 13, 995 - 8.

(67). Shotton, E., and Davis, S.S., 1967, J. Pharmacol., 19, 1305.

Idem, ibid, 1968, 20, 780 - 9.

(68). Barnes, S., et al., 1966, Brit. J. Appl. Phys., 17, 1501 - 1506.

(69). Kellie, J.L.F., 1966, Proc. of 4th British Coulter Counter users Assoc., Bradford, U.K.

(70). Shrenzel, M., 1966, Pharm. Acta. Helv., 41, 218 - 227.

(71). Short, P.M., and Rhodes C.T., 1969, Die. Pharmazie, 6, 319 - 322.

(72). Marshall, K., 1969, "The Reduction and Presentation of Coulter Counter Data", Conf. on use of Coulter in Pharmaceutical Industry, Basle.

(73). Mathews, B.A., 1971, Can. J. Pharm. Sci., 6, (2), 29 - 34.

(74). Tech. Bulletin, 1971, "Electrozone Computerised Particle Data Processing System", Particle Data Inc., P. O. Box 265, Elmhurst Ill., 60126 U.S.A.

(75). Stull, N.R., 1975, Hydraulics and Pneumatics, June.

(76). Tech. Bulletin, 1973, Allied Chemical (Plastics Division), S.A. Tech. Service Centre, P. O. Box 2365 R, Morristown, N.J.

(77). Tech. Bulletin from Hoechst Waxes issued at "Waxes and Additives", symp. 10th May 1973.
W250 C (March 1973); W240/1 (Dec. 1971); W48/9C (Feb. 1972); 523C (April 1973); W129/4 (1970); A 84C (Nov. 1972); W 248C (April 1977).

(78). Tech. Bulletins from Eastman Chemicals (undated).
TD5 No. F-128.
TD5 No. F-152.
F-165C.
F-240.

(79). Tech. Bulletins from Petrolite Waxes, Rev. 1 - 70, Bareco Division, Tulsa, Oklahoma.

(80). Lange, J. et al., 1967, Fette Seifen Anstrichm., 69, (10), 718 - 724.

(81). Lange, J., et al., 1966, Soap and Chem. Specialities, May, 115 - 140.

(82). Idem, ibid, June, 91 - 96.

(83). Von Bramer, P.J. and McGillen W. D., 1966, ibid Dec., 123.

(84). Johnson, L.P., and Draper, W.E., 1975, Soap and Chem. Specialities, Dec., 123 - 145.

(85). Richardson, E.G., 1950, J. Colloid Sci., 5, 404 - 413.

(86). Rowe, E.L., 1965, J. Pharm. Sci., 54, (2), 260 - 264.

(87). Pickthall, J., 1955, Soap Perfumery Cosmetics, 28, 69 - 75.

(88). Roger, W.A., et al., 1956, Chem. Eng. Prog., 52, (12), 515 - 520.

(89). Fondy, P.L., and Bates, R.L., 1963, A.I.Ch.E.J., 9, (3), 338 - 342.

(90). Hackett, W.J., 1972, "Maintenance Chemical Specialities". Chem. Publishing Co., N.York.

(91). Clayton, W., 1919, J. Soc. Chem. Ind., 38, (10), 113T - 118T.

(92). Idem, 1932, Chem and Ind., 51, (2) 129 - 139.

(93). Bancroft, W.D., 1913, J.Phys.Chem., 17, 501.

Idem, 1915, ibid, 19, 275.

(94). Lewis, W.C., 1909, Kolloid - Z, 4, 211.

(95). Harkins, W.D., and Fischer, E.K., 1932, J. Phys. Chem., 36, 98.

(96). Stamm, A.J., and Kraemer, E.O., 1926, J. Phys. Chem., 30, 992 - 1000.

(97). Finkle, P., et al., 1923, J. Amer. Chem. Soc., 45, 2780 - 2783.

(98). Thomas, A.W., 1920, J. Ind. Eng. Chem., 12, 177 - 181.

Idem, 1920, J. Amer. Leather Chem. Assoc., 15, 186 - 201.

(99). Sumner, C.G., 1960, Paint Technol., 24, (266), 14 - 34.

(100). Bancroft W.D. and Tucker, C.W., 1927, J. Phys. Chem., 31, 1680.

(101). Harkins, W.D., 1952, "The Physical Chemistry of Surface Films", 83 - 91, Reinhold Publishing Corp., N.York.

(102). Hilderbrand, J., 1924, "Colloidal Behaviour", 1, 212, Bogue, N.York.

(103). Stamm, A.J., and Svedberg, J., 1925, J.Amer. Chem. Soc., 47, 1582 - 1596.

(104). Leslie, R., 1947, Mfg. Chemist, 18, (11), 494 - 499.

(105). Figliolino, A., 1951, Paint and Varnish Production, 31, (1), 14 - 17.

(106). Warth, A.J., 1947, "The Chemistry and Technology of Waxes", Reinhold Pub. Corp., N.York.

(107). Davidsohn, A., 1956, "Polishes and Cleaning Material", L. Hill Books Ltd., London.

(108). Jarden, R., 1941, Soap and Sanitary Chems., 17, (3), 90 - 117.

(109). Sweet, R. S., 1970, Soap and Chem. Specialities, May, 55 - 56 and 115.

(110). Brunson, M.O. and Queen, C.D., 1960, Ibid, Oct., 82 - 84.

(111). Brunson, M.O., and Dickert, J.E., 1962, Ibid, Sept., 91 - 93, and 118.

(112). Law, J.A., 1965, Chem. and Ind., Jan., 171 - 172.

(113). Glas, B., et al., 1973, Labo-Pharma., 21, (224), 39 - 84.

(114). McQuillan, P.G., and Gregg, S.J., 1965, Soap and Chem. Specialities, Nov., 387 - 390 and 392.

(115). Hunsucker, J.H., 1971, Soap and Chem. Specialities, May, 51 - 52, and 91.

(116). Glaub, W.R., 1971, U.S. Patent 3,579, 461.

(117). Peck, G.E., et al., 1960, J. Amer. Pharm. Ass., 49, (2), 75 - 79.

(118). Ashley, M.J., 1974, The Chem. Engr., 74, (286), 368 - 371.

(119). Powley, C., 1973, Process Eng'g., April, 101 - 103.

(120). Marshall, K., 1965, Soap, Perfumery, Cosmetics, Sept., 759 - 768.

(121). Hough, J.D., 1976, Univ. Aston Dept. of Chem. Eng'g., Project Report.

(122). Private communication with Allied Chemical.

(123). Private communication with Hoechst waxes.

(124). Stavridis, C.G., 1975, Unv. of Aston, M.Sc. Thesis entitled "Identification of Key Raw Materials for Johnson Wax Ltd.

(125). Vickers Instruments Ltd., 1977, Manual for M - 17 Optical Microscope.

(126). Coulter Electronics Ltd., Harpenden, Feb. 1975, "Instruction Manual for Coulter Counter Model ZB (Industrial), 3rd Edition.

(127). H. Simons, (Filter Cloths) Ltd., P.O.Box 31, Stockport, Cheshire.

(128). Coulter Electronics Ltd., Harpenden, Dec. 1974, "Instruction Manual for Coulter Counter Model T.A.

(129). Stokes, G.G., 1851, Trans. Cambridge Phil. Soc., 9,.

(130). Rybczyski, W., 1911, Bull, Acad. Sci. Cracovie, 40.

(131). Hadamard, J., 1911, Compt.rend., 154, 1735.

(132). Franklin, A.N., and Levich, V.G., 1947, Zhur. fiz. khim., 21, 1183.

(133). Levich, V.G., 1962, "Physicochemical Hydrodynamics",402 - 404, Prentice - Hall, Inc., N.York.

(134). Brookfield Eng'g. Labs., Inc. Instruction for LVT.

(135). A.S.T.M. D127-63, 1968, "Standard Method of Test for Drop Melting point of Petroleum Wax", A.S.T.M. Book of Standards, Part 18.

(136). Johnson Wax Ltd., - Product Formulation Files.

(137). Private communication with Hoechst Waxes.

(138). Private communication with Premier Colloid, Walton-on-Thames, U.K.

(139). Rushton, J.H., et al., 1953, Chem. Eng. Prog., 49, (161), 767.

(140). Quinke, G., 1870, Pogg. Ann., 139, 1.

(141). Donnan, F. G., and Potts, H.E., 1910, Kolloid - Z, 7, 208.

(142). Van den Tempel, M., 1953, Rec. trav. chim., 72, 419.

(143). Albers, W., and Overbeek, J.Th.G., 1959, J. Colloid Sci., 14, 501.

(144). Janovsky, W., and Pohlman, R., 1948, Z angrew. Phys., 1, 222.

(145). Nawab, M.A., and Mason, S.G., 1958, J. Colloid Sci., 13, 179 - 187.

(146). Ruston, J.H. et al., 1950, "Power characteristics of mixing Impellers, - Part I", Chem Eng. Prog., 46, (8), 395 - 404.

Idem, ibid, Part II, 46, (9), 467 - 476.

(147). Du Nouy Tensiometer Instruction Manual.

(148). Matsumoto, S., and Sherman, P., 1969, J. Colloid and Interface Sci., 33, (2), 294 - 298.

(149). Parkinson, C., and Sherman, P., 1971, Ibid, 41, (2), 328 - 330.

Idem, 1977, Colloid Polymer Sci., 255, 172 - 173.

(150). Eastman Chemicals, April 1977, Epolene E 43 Polyethylene Waxes.

14

Wax Emulsions: Formation and Manufacture

A. V. BRIDGWATER
University of Aston in Birmingham, England

J. M. C. ROBERTS
Johnson Wax Ltd, Frimley Green, Camberley, Surrey, England

Abstract

An introduction to wax emulsion is given followed by a survey of theory, formulation and manufacturing practice. The essential requirements of a wax emulsion are identified and exemplified by reference to several products. An attempt is made to classify these requirements and hence evaluate alternative modes of formation and formulations. As well as relating these to current industrial practice, suggestions are also made about possible future trends.

1 Introduction

Wax emulsions are an accepted and familiar part of domestic life. They have evolved over many years from relatively coarse suspensions of natural wax stabilized with natural emulsifying agents to present-day formulations containing up to twenty or more man-made and treated natural materials, dispersed as near colloid-sized particles.

This paper is concerned with wax emulsions where one of the major constituents is water and the "oil" phase may be liquid or solid. There are other wax-containing products, not included here, where the wax is either dissolved in a suitable solvent, or suspended in a saturated solution as a dispersion which may take the form of a liquid or paste. The basic objective of an emulsion is to achieve a desired effect in the most economical way by using one of the cheapest raw materials available—water.

A wax emulsion consists essentially of water, wax and an emulsifying agent. There are so many different types and grades of wax and emulsifying agents available that no attempt can be made to include comprehensive coverage. Information is available from the material suppliers, standard textbooks and the technical literature, both for waxes [1, 9, 13, 14] and emulsifying agents.[2, 3, 9, 11]

2 Background

The manufacture of wax emulsions has evolved as an art rather than a science where a successful product is made by following a "recipe". Any development in wax emulsion technology therefore tends to follow the "trial and error" approach.

Emulsion science in general is well advanced and documented, where emulsions are regarded as composed of two liquids. However, it is not clear whether wax emulsions are true emulsions in this sense, as waxes are usually solid at ambient temperatures. There is some evidence that wax emulsions above a certain particle size may really be dispersions of finely divided solid in an aqueous phase.[4, 5] Below this particle size, which is believed to be around 20–40 μm, the wax may form a liquid or semi-liquid droplet with the emulsifying agent. This suggestion is supported by experience in manufacturing wax emulsions. If a coarse emulsion (of particle size above that indicated) is formed as a result of operating error, it has been found impossible to reduce the particle size by the input of any amount of energy, and the emulsion either has to be discarded or reworked by a pressure emulsification technique when a liquid wax–liquid water system is re-emulsified.

There is some doubt therefore whether the classical theories of emulsification—the interfacial tension theory and orientation theory—may be applied to wax emulsions. Since these theories are already well documented, there is no need for them to be reproduced.

The mechanism of formation of a satisfactory emulsion depends not only on the materials employed, but also on the manufacturing variables and the definition of "satisfactory". The art of producing an acceptable emulsion is known, but little attention has been paid to the interdependence of manufacturing variables and their effect on the final product. Lange *et al.*[6, 7] have carried out some interesting work in relating two floor-care product qualities, viscosity and dry bright effect, to seven major manufacturing variables: melting time, wax temperature, water temperature, water hardness, stirring speed, cooling time and emulsification time. They used a simple threecomponent mixture to minimize material interaction, and produced two equations relating dry bright effect and viscosity to melting time, wax temperature, water hardness, cooling time and emulsification time. Water temperature and stirrer speed were found to have a negligible effect. This is contrary to the authors' experience, and also draws attention to the problem of defining a satisfactory product in that the two properties correlated do not constitute an adequate product specification.

Work is progressing on the development of an acceptable theory of formation so that significant factors in manufacture may be identified and quantified. To date it is possible to range the manufacturing variables qualitatively in approximate descending order of importance for atmospheric and pressure emulsification in producing a self-polishing (dry bright) floor polish:

Atmospheric	*Pressure*
Wax temperature	Water content of "water in wax" initial melt
Water temperature	
Rate of agitation	Rate of addition of "cold" water
Rate of wax addition	Temperature of "cold" water
Emulsifier concentration	Rate of agitation
Time of holding emulsion	Emulsifier concentration
Time of holding wax hot	Rate of cooling
Rate of cooling	

It is also important to be able to specify the qualities of a satisfactory product. For a self-polishing floor-care emulsion the following are suggested[1]: initial gloss, buffed gloss, recoatability, film clarity, discolouration, water resistance, film flexibility, film adhesion, levelling, removability, wearing properties, tack, black heelmark resistance, powdering, compatibility, slip retardance, stability, no streaking,[9] no crazing,[9] no film clarity.[9] In addition the coating should dry easily, have good resistance to scratching, scuffing and detergents, and be easy to recoat or repair.

There is likely therefore to be considerable difficulty in quantifying the acceptability or otherwise of any given product. Certain tests are available[8, 15] for many of the above properties, both individually and collectively, e.g. by light transmission,[10] but ultimately the success of the product will depend on customer acceptance. The criteria for assessing the performance of any product therefore tends to be subjective and variable with time.

3 Formulations

There are seven major end-uses of wax emulsions: floor-care products, furniture and multisurface polishes, autocare products, paper coatings, fruit coatings, ropes and textiles, cosmetics. Although most experience has been gained in the first three types of product, all are included for comparison.

3.1 FLOOR-CARE PRODUCTS

There are basically two types of floor-care products: buffable and self-polishing. The former may be manually or mechanically applied, left for 15–30 minutes for water loss by evaporation, then mechanically buffed to produce a durable gloss film. A fairly hard wax blend (petroleum, polyethylene, and montan) and careful control of particle size is necessary. The wax blend and balance of resin and plasticizer is particularly important in order to give the properties shown in Table 1.

Table 1
Floor-care products: typical formulation and properties

Material	Purpose	Approximate % w/w Buffable	Approximate % w/w Self-polishing
Wax emulsion 20% solids	Provide wax film, modify polymer film	56	13
Metallized acrylate polymers	Produce air-drying film to complement wax and resin		35
Neutralized resin solution	Improve spreading, levelling and gloss	17	5·6
Plasticizer	Improve gloss, slip resistance, levelling	0·3	
Levelling agent (fluorchemicals)	Control levelling to avoid streakiness		1·2
Surfactant	Improve storage, stability and spreadability		1·0
Bactericide	Prevent biodegradation	0·1	0·2
Water	Diluent	26·6	44

The advantages and disadvantages of the two types of product to consumer and manufacturer are summarized in Table 2.

The self-polishing, or dry bright product, has merely to be applied and left to dry. Similar modifiers to the buffable product are required for the same purpose. The acrylate polymers complement the wax film to produce a gloss finish without working. Detergent resistance is

Table 2
Advantages and disadvantages of floor-care products

	Advantages	Disadvantages
A. Buffable		
To consumer	Low cost. Repair by re-buffing. Need for "working" satisfied	Requires considerably more time to treat and maintain large areas. Lower durability. Less "customer proof". Successive coats build-up and reduce floor appearance
To manufacturer	Does not require sophisticated production equipment. Freedom from foaming during processing and filling	Requires more expensive and difficult to obtain waxes. Not compatible with self-polishing products.
B. Self-polishing		
To customer	Minimizes labour requirements and costs of treating large areas. Produces a hard, durable, slip-resistant, gloss finish. Floor appearance improves with successive coats. Virtually "customer proof"	Higher cost. Stains difficult to remove.
To manufacturer	Ready availability of synthetic waxes (prior to oil crisis). Increased sales due to "easier to use product"	Requires more sophisticated production equipment. Requires more expensive packaging. Problems of foaming and rapid air drying during handling. Raw material supply problems (post oil crisis)

a relatively new requirement which is achieved by adding controlled amounts of a zinc ammonium carbonate complex which ties up the free carboxyl groups in the acrylate or styrene acrylate polymer system, thus preventing any reaction with alkaline cleaning agents. The reaction is conveniently reversible in the presence of ammonia which may be used to remove the film.

There are formulations giving products of intermediate properties to those described above. These tend to combine the disadvantages but not advantages.

Clear self-polishing products have been developed using polyethylene waxes, and producing a high-purity emulsion with very small particle sizes.[16]

3.2 FURNITURE AND MULTISURFACE POLISHES

These are usually produced as aerosols and are intended to clean as well as provide decorative and protective coatings for manufacturers' permanent finishes. These emulsions are relatively coarse and unstable compared to self-polishing floor-care products. The particle size usually lies between 10 and 30 microns. The instability is intentional so that the polish will "break" when mild mechanical abrasion is applied via the dusting cloth on the surface. During this wiping action the wax, silicones and oil are transferred to the surface, and the dirt dust and moisture are taken up by the cloth, leaving an "instant shine". The manufacturing technique, atmospheric, indirect, is water to wax for furniture polish and wax to water for multisurface polish. The desired properties for furniture polishes are: high gloss and surface protection with minimum effort, easy application, rapid drying time, minimum drag on cloth, absence of smears and resistance to marks and abrasion. For multisurface polishes should be added versatility for use on almost any surface and lower cost. Table 3 gives typical formulations.

Table 3
Furniture and multisurface polish: formulation and properties

Material	Purpose	Approximate % w/w	
		Furniture	Multisurface
Soft water	Diluent	72	69
Petroleum hydrocarbon solvent	Solvent, and to form emulsion	20	22
Technical white oil	Cleaning solvent	0·5	
Silicone fluids	Gloss and drag modifiers	4·0	5·5
Beeswax	Form protective film	1·7	
Microcrystalline–paraffin wax blend	Form protective film		1·3
Emulsifers	Form stable emulsion and assist cleaning	1·0	1·4
Perfume		0·4	0·8
Bactericide	Prevent biodegradation	0·2	0·3
Butane	Propellant	—	—

3.3 AUTO-CARE PRODUCTS

There are four types of product manufactured: liquid polish, gel (or paste) polish, shampoo and chrome cleaner. The object of all these polishes is to remove the oxidized (paint) film and road dirt, provide a durable and detergent-resistant gloss with the minimum of effort, and to impart water resistance.

The two polishes are effectively identical and merely cater for customer preference. The polish is applied directly as liquid, or with a damp cloth from the gel formulation, and allowed to dry. This deposits a layer of thickened wax emulsion, abrasives and detergents on the paint surface. This is buffed with a dry cloth which removes the traffic film and oxidized paint film by mild abrasion and detergent cleaning, and leaves behind a water-resistant, glossy wax film. The formulations are given in Table 4.

Table 4
Car polish formulations

Material	Purpose	Approximate % w/w Liquid	Gel
Carnauba–paraffin microwax blend emulsion	Provide protective film and impart gloss	80	70
Silicone fluids	Reduces drag and assists in gloss finish and water resistance	5·5	5·6
Abrasive	Removes dirt and traffic film	10	10
Thickening agent	Suspends abrasive	4·5	14·2
Perfume		0·2	0·2
Dye		0·04	0·04
Bactericide		0·1	0·1

For car shampoos the current trend is for a "wash and shine" product. This is diluted and used to wash the car free from road dirt. Hosing or wiping off with cold water removes the detergent and dirt leaving behind a wax film which imparts gloss and water resistance. The same wax emulsion as that used in polishes is employed and constitutes 10 per cent by weight of the product. The wax emulsion in chrome cleaners is a minor constituent (5 per cent) which provides a protective film, and enhances gloss and water resistance.

3.4 PAPER COATINGS

Wax emulsions are used in the paper industry for both sizing and coating. Traditionally carnauba and paraffin wax emulsions were used, together with clays, talc, casein, glue and water. This fills and coats any interstices between the cellulose fibres. The wax content reduces water absorption and transmission. Due to economic factors, polyethylene waxes are now preferred, and the wax emulsion part of the sizing solution has the approximate composition:

	% w/w
Polyethylene wax	18
Paraffin wax	2
Emulsifier	4
Potassium hydroxide	0·1
Softened water	75·9

Similar emulsions are used in the textile and leather industries.

Waxes are used in paper coatings also to increase surface gloss and printability. The wax is applied as an emulsion of typical composition:

	% w/w
Montan–polyethylene wax blend	20
Emulsifier	4
Softened water	76

Pigments such as titanium dioxide and other additives may be applied simultaneously.

3.5 FRUIT COATINGS

Citrus fruit and dessert fruit are often produced at a considerable distance from their market. Spoilage can be unacceptably high, due to handling and desiccation during transport. A protective wax coating round the fruit reduces water loss, improves stability, and is claimed to reduce fungal and bacterial attack. The wax also improves the appearance of the fruit.[18]

Application is by spraying or dipping the fruit in a wax emulsion. Natural waxes such as carnauba and other vegetable waxes were traditionally used, but due to economic and supply factors, polyethylene wax is now also being employed. There is strict legislation in many countries governing the composition and use of such emulsions, notably that of the FDA (USA) and Federal German Food Laws. Certain Montan waxes meet the specifications of the above two authorities, but polyethylene waxes are not always as acceptable. Typical formulations are:

	% w/w
Montan wax	11
Olein (emulsifier)	4
Morpholine or AMP (emulsifier)	3
Sodium hydroxide	0·3
Water	81·7

or

Polyethylene wax	16
Olein	4
Morpholine or AMP	4·8
Water	75·2

The application is very economical—1 gallon is often sufficient for up to 8000 fruit.

Polyethylene wax emulsions of 20 per cent w/w solids content are also used to spray young plants in hot countries to prevent excessive water loss. The choice of emulsifier is important to avoid toxic effects.

3.6 ROPES AND TEXTILES

A 20 per cent w/w polyethylene–paraffin wax emulsion is applied to sisal and other natural fibre ropes to provide flexibility and lubrication both during manufacture and use. The wax also helps make the rope water resistant and hence reduces rotting.

3.7 COSMETICS

Waxes and wax-like materials are extensively used in cosmetics. It has been estimated that 25 per cent of cosmetics contain wax, and that the industry is the largest consumer of beeswax.[17] Other waxes and wax-like materials used include lanolin, spermaceti, ozokerite, paraffin, microcrystalline, montan wax derivatives, and waxy alcohols.

Generally, cosmetics are intended to either cleanse and/or allay skin troubles and/or camouflage imperfections. They may also act as carriers for medication. There are so many variations that the subject cannot be adequately dealt with in this paper, beyond a brief classification:

Emollient creams and lotions are used to prevent or treat dryness, or as a cream base for medication. The following waxes are widely employed: petrolatum, paraffin, ceresin, ozokerite, microcrystalline, polyethylene and derivatives of beeswax. The wax content is usually 10–20 per cent.

Cleansing creams are used to remove facial make-up, surface grime and oil. Blends of beeswax, spermaceti and ozokerite waxes are often employed and constitute up to 20 per cent of the cream or lotion. Mineral oil is usually the major constituent, around 50 per cent and is included for its cleansing action.

Hand creams and lotions are used to soften and cleanse the skin, and also act as emollients. Waxes usually only have significant use in barrier creams, when petrolatum, paraffin wax and ozokerite are employed.

Make-up is available in a wide range of products. Considerable care in formulation is necessary to avoid irritation, side effects and toxicity.

Embalming preparations are used as wound fillers to make the corpse appear more "natural". These products are based on beeswax–paraffin wax blends, emulsifiers with a soap system and thickened with Bentonite.

4 Formation

4.1 PRESENT

There are three basic methods of making wax emulsions which are all usually batch techniques:

1. Water to wax, forming a water-in-wax emulsion which inverts as the water concentration increases.
2. Wax to water, either to the surface or below the surface.
3. Pressure emulsification, where the wax and water are both liquid and a high solids content emulsion is formed under pressure and high temperature. This is diluted and cooled with "cold" water to give the desired product.

These methods may be supplemented with ultrasonic emulsification equipment, which requires some premixing and therefore cannot be used by itself.

Water-to-wax emulsions may be made by either adding hot water to melted wax which is a critical technique and is limited to low melting point waxes often producing cosmetic preparations, or by adding hot or cold water to a hot solution of the wax in solvent. This latter technique is used for manufacturing furniture polishes which contain a solvent in the formulation (q.v.). Problems can arise with products containing a low proportion of solvent which makes the wax solution very viscous and difficult to agitate during water addition. Particle size is also critical as the emulsions are frequently used in aerosols and blockage can occur under adverse conditions of high particle size and instability.

Wax to water methods are the most widely employed and the specific mode of formation is very dependent on the materials used in the formulation. Generally wax is melted together with one or more of the emulsifying agents and/or additives and is poured into hot water which contains the rest of the emulsifiers and/or additives. The wax may be added to the surface of the aqueous phase or below the surface into the eye of the stirrer. The rate of addition of wax, amount of energy input and type of agitation are specially important for both techniques, but particularly the first. This general method may also be used for premixing with final emulsification by ultrasonics. The equipment is described in reference 12.

Pressure emulsification is effected by placing the waxes, emulsifiers, additives and about 10 per cent of the water in a pressure vessel. The temperature is raised to around 10°C above the melting point of the highest melting point wax and the mixture is agitated. The pressure is usually between 30 and 50 lb in^{-2}. A water-in-wax emulsion of approximately 60 per cent solids is formed, which is inverted by injecting preheated water and agitating thoroughly to give a wax-in-water emulsion of the required solids content. This technique is most useful for waxes having a melting point higher than 100°C and also for reworking poorly constituted emulsions. There are many advantages to pressure emulsification in that only one vessel is required, there is no loss of additives by evaporation, better control is possible, and the time required is about one fifth of that required for the atmospheric method. Pressure emulsification is now used almost exclusively in the USA.

4.2 FUTURE

Practically all wax emulsions are manufactured batchwise by one of the above three methods. This is considered as partly due to the "art" of manufacture, and partly due to the very large number of products made of widely variable formulation from a limited range of equipment. There are few products made in sufficient quantity to warrant an in-line mixing/blending operation. One possibility, however, would be to make a standard high solids content emulsion which might serve as a base for a range of products, diluted and/or added to as necessary. A continuous version of pressure emulsification could be developed for this purpose. It is conjectural at this stage what economies might be achieved by such practice, or whether a suitable base emulsion could be formulated.

As a result of rapidly changing consumer requirements and free competition, it is difficult to see any significant change taking place in manufacturing practice beyond those described above. Manufacturers will probably continue to employ the basic techniques using a limited range of equipment that will have a reasonable serviceable life. There are likely to be relatively minor developments, for example in rapid wax melting equipment and agitator design. In-line mixing and blending is also under active consideration.

The other significant change may be brought about by raw material supplies. Natural waxes are not only substantially increasing in price but also becoming difficult to obtain. Synthetic waxes such as polyethylene waxes are tending to follow a similar pattern. The more readily available and cheaper waxes such as montan and paraffin may find increasing usage, and as these may be handled by atmospheric techniques further development may be in this direction. For manufacturers with a heavy commitment in pressure equipment, development in handling these wax blends is necessary.

5 Conclusions

An attempt has been made to summarize the state of the art of making wax emulsions by reference to manufacturing practice and formulations. Little work has been performed to date on relating manufacturing variables to final product specification, which is at least partly attributable to the difficulty of adequately specifying a satisfactory product. The future is likely to be one of rapidly changing formulations to meet consumer needs with little change in manufacturing practice but subject to raw material supplies.

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References

1. Law, J. A. (Jan. 23, 1965). *Chem. Ind.*, 171.
2. Law, J. A. (June. 1970). *Detergents and Specialities*, 30.
3. Chalmers, L. (Aug., 1971). *Paint Mfr.* 30.
4. Parfitt, G. M. Project report, University of Aston.
5. Parfitt, G. M. Allied Chemicals technical literature.
6. Lange, J., Malitschek, O. and Jochinke, H. (May, 1966). *Soap Chem. Spec.* 115.
7. Lange, J. and Jochinke, O. (1967). *Fette Seifen. Anstrichm.* 69, no. 10, 718.
8. Lange, J. and Jochinke, O. (Jan., 1967). *Soap Chem. Spec.* 116.
9. Hopper, T. R. (Oct., 1970). *Soap Chem. Spec.* 36.
10. Queen, L. D., Brunson, M. O. and Johnson, L. P. (Mar., 1964). *Soap Chem. Spec.* 99.
11. Brunson, M. O. and Queen, L. D. (Oct., 1960). *Soap Chem. Spec.* 82.
12. Ashley, M. J. (June, 1974). *Chem. Engr.* 368.
13. Warth, A. H. (1956). "The Chemistry and Technology of Waxes". Reinhold, New York.

14. Hackett, W. J. (1972). *Maint. Chem. Spec.* 243–263.
15. Hackett, W. J. (1972). *Maint. Chem. Spec.* 110–154.
16. Hackett, W. J. (1972). *Maint. Chem. Spec.* 14–21.
17. Hackett, W. J. (1972). *Maint. Chem. Spec.* 236.
18. Dalal, V. B., Eipeson, W. E. and Singh, N. S. (Sept./Oct., 1971). *Indian Food Packer,* **25**, no. 5, 9–15.

APPENDIX II

SMLRP (SMLRPOBJ)

SMLRP (Stepwise Multiple Linear Regression Program) computes in a stepwise manner the least squares "best" value for the coefficients of an equation of the form:

$$Y = B_0 + B_1X_1 + B_2X_2 + \ldots + B_nX_x$$

where Y is the dependent variable; X_1, X_2, . . . , X_n are the independent variables; and B_0, B_1, B_2, . . . , B_n are the coefficients to be determined. The program also provides statistical measures of the reliability of the computed coefficients.

SMLRPOBJ is the compiled object version of this same program.

PROGRAM FEATURES

- Program handles up to 20 variables.
- Ability to identify the problem data file at run time.
- Stepwise addition and deletion of independent variables based on the critical F-statistic.
- Optional printout of means, standard deviation, and correlation matrix.
- User selection of dependent and independent variables at run time.
- Optional stepwise results.
- Free-field data input.
- Variable transformations on input data.
- Ability to force variables into the regression.
- Optional residual summary.
- Option of entering the critical F-value or the confidence level.
- User provided variable labels.

METHOD

The program performs the stepwise regression analysis, using the matrix of simple correlation coefficients. Any combination of one dependent variable and one or more independent variables may be selected for analysis from the input or transformed variables.

In the stepwise procedure, independent variables are added one at a time to the regression, giving the following intermediate equations:

$$Y = B_0 + B_1X_1$$

$$Y = B'_0 + B'_1X_2 + B'_2X_2$$

$$Y = B''_0 + B''_1X_1 + B''_2X_2 + B''_3X_3$$

In this manner, it is possible to obtain valuable statistical information at each step of the calculation.

At each step, those independent variables not included in the regression are inspected to find the one that will give the greatest reduction in the variation of Y. This variable is then tested for significance; i.e., the computed F-ratio of the variable is compared to the supplied critical F-value. If the computed value is greater than the critical value, the variable is considered significant and is added to the regression solution.

After each new variable has been added, those variables already in the regression are inspected to see if any of them can now be deleted because their contribution to the reduction in the variation of Y is no longer significant. Those variables which have a computed F-ratio less than the critical value are considered insignificant ana are deleted from the regression solution.

This process is continued until no more variables can be added or deleted. Thus, the final regression solution contains only those variables that are statistically significant (except forced variables).

Under user control, it is possible to force one or more of the independent variables into the regression solution. These variables are added to the fit, before any other variables, with no regard for statistical significance. The remaining independent variables are then added to the fit in the normal stepwise procedure as outlined in the preceding paragraphs. However, once a variable has been forced into the regression, it will not be deleted in the following steps even though it is not statistically significant.

DATA PREPARATION

Before running the program, the user should go into the EDIT Subsystem and enter the problem data into one of his own files in free-field format.

NOTE:

Line numbers must not be used, which is the reason for using the EDIT Subsystem.

General rules for free-field input are:

1. Data entries are separated by one or more blanks, or a comma.
2. Blanks preceding a data field are ignored. The first blank following a data field terminates the field. The combination of a blank followed by a comma is treated as a null field and must be avoided.
3. To repeat a numeric value, enter the repetition count followed by an asterisk (*). The asterisk is then followed by the numeric value to be repeated, i.e., 4*3.2.
4. The following input formats are acceptable for the number twenty-five:
   (a) 25
   (b) 25.0
   (c) 2.5E1
   (d) .25E+2
   (e) 250E-1

The first line of the problem data file contains the total number of input variables, which is limited to 20. The observed data follows next and is entered by observations (row-wise): that is, each record contains an entry for X_1, X_2, X_3, . . . , X_n. Each observation must begin on a new line. All the data values for an observation are assumed to be contained on a single line unless that line ends with a comma followed by a carriage return. When it does, the next line is considered a continuation of the first line.

Since there is no special end of data flag, the user should ensure that no extraneous information follows the last observation for the current problem. The maximum number of observations is limited to 999.

See the following sections for optional transformations and variable labels.

After all the data has been entered and checked for accuracy, the file should be saved.

DATA TRANSFORMATIONS

The program provides the option of performing transformations on the raw variable data. The user performs these transformations by entering in the data file a series of pseudo-codes which logically produce the desired transformations on the specified variables.

To use the transformation option, the second line of the data file must contain the alphabetic word "TRNF" followed by the total number of variables after all transformations have been performed.

The transformation codes are entered one per line following the line containing "TRNF", and are of the following general form:

OP I J K

where OP is the three character alphabetic transformation code, I and J are the indices of the variables to be operated upon, and K is the index of the resulting variable. Most transformation codes operate on only one variable, and in these cases, a dummy index of '1' must be used in the position of the index that will not be used.

The index of a given variable is simply its position with respect to the other variables. For example, the third variable has an index of 3. The program provides 10 pseudo variables with indices of 21-30 that may be used for storage of intermediate results. However, the final index of a transformed variable may not exceed 20. A description of the transformation codes follows:

1. Two-Operand Codes

CODE				MEANING
ADD	I	J	K	$X_i + X_j \longrightarrow X_k$
SUB	I	J	K	$X_i - X_j$ -- X_k
MPY	I	J	K	$X_i * X_j$ -- X_k
DVD	I	J	K	X_i/X_j -- X_k

2. One-Operand Codes

RCP	I	K	1	$1.0/X_i$ -- X_k
MOV	I	K	1	X_i -- X_k
EXP	I	K	1	e^{X_i} -- X_k
TEN	I	K	1	10^{X_i} -- X_k
LGN	I	K	1	LOG_e (Xi) -- X_k
LOG	I	K	1	LOG_{10} (Xi) -- X_k
SIN	I	K	1	Sine (Xi) -- X_k
COS	I	K	1	Cosine (Xi) -- X_k
TNH	I	K	1	Hyperbolic Tangent (Xi) -- X_k
SQR	I	K	1	Xi -- X_k

3. Terminating Code

END 1 1 1 last line of transformation codes.

The observed variable data or variable labels start on the next line following the "END" code.

A special transformation code permits the use of constants in the transformation manipulations. This special code has the form:

CON I constant value 1

where I is the index (21-30) of one of the pseudo variables. The appended power of ten exponent (E) is not permitted for the constant value.

An example of transformation coding would be to evaluate the expression:

$$X_{13} = X_1 - 3(X_3)^2 + LN(X_2 - X_4)$$

The following lines would be required:

TRNF	13			
CON	21	-3	1	$-3.0 \text{ -- } X_{21}$
MPY	3	3	22	$(X_3)^2 \text{ -- } X_{22}$
MPY	21	22	22	$-3(X_3)^2 \text{ -- } X_{22}$
SUB	2	4	13	$(X_2 - X_4) \text{ -- } X_{13}$
LGN	13	13	1	$LN(X_2 - X_4) \text{ -- } X_{13}$
ADD	22	13	13	$-3(X_3)^2 + LN(X_2 - X_4) \text{ -- } X_{13}$
ADD	1	13	13	$X_1 - 3(X_3)^2 + LN(X_2 - X_4) \text{ -- } X_{13}$
END	1	1	1	

VARIABLE LABELS

As an option, the user may provide meaningful labels or names for each of the final variables. If present, these labels are included in the printed results for each variable. The labels are entered in the data file following the transformation coding (if present) and preceding the observed data.

The label names may consist of one to four characters, the first of which must be alphabetic. The remaining characters of the label may be any character with the exception of the comma (,), quote mark ("), exclamation mark (!), or embedded blank.

First, a line containing the entry "LABL" and the number of labels is made (e.g., LABL 11). This is followed by the line of label names, which <u>must</u> end with the entry "ELAB" (e.g., X1, X2, X3, Y4, Y5, ELAB). This line may be continued to the next by ending it with a comma.

The number of labels may not exceed the number of final variables. However, fewer labels than variables are acceptable, in which case the labels for the remaining variables are blank.

OPERATING INSTRUCTIONS

1. The user should first establish and save the data file. The program can then be executed by running either the source version SMLRP or the object version SMLRPOBJ. For example, to run the object version, the user could type:

```
GET    LIBRARY/SMLRPOBJ,R

RUN    SMLRPOBJ
```

2. The program responds by asking the user to enter the name of his data file. The program then prints the number of initial variables, the final number of transformed variables, and the number of observations.

3. The user is then asked to enter "YES" or "NO" (Y or N is sufficient) for the optional printout of the mean, standard deviation, minimum value, and maximum value for each variable.

4. Next, "YES" or "NO" is requested for the printout of the lower half of the simple correlation matrix.

5. The user is next requested to enter the number of independent (X) variables to be considered, then the index of the dependent (Y) variable, followed by the indices (in any order) of all the independent (X) variables. The index of any variable is simply its position with respect to the other variables. If the index of any independent variable is entered as a negative value, that variable will be "forced" into the regression. This option should be used with discretion, and only those variables known to be significant by some prior knowledge or theory should be forced. If any input errors are detected, such as an index larger than the total number of variables, an incorrect number of indices, or a conflict between the index of the Y variable and that of one of the X variables; the input is requested again.

6. Next, a request is made to enter a "F" or "CL", indicating whether the user is going to supply the critical F-value of the confidence level. The indicated value is then requested. If the confidence level is entered, the program will compute the critical F-value at each step of the regression.

7. The user is then asked to answer "YES" or "NO" to whether full results are to be printed at each step of the regression.

8. The program then proceeds with the stepwise regression analysis. First, a line is printed listing the data file name, the identification of the dependent variable, the confidence level (CL), the degrees of freedom (DØF), and the residual sum of squares (RSS). Initially RSS equals the total sums of squares of the dependent variable.

At each step of the regression, the following summary is printed: The number of the step, the identification and label of the independent variable preceded by a "+", "-" or "*" (indicating the variable was added, deleted or forced), DØF, the coefficient or multiple determination (R^2), and the standard error of the estimate (SEE).

Depending on the option taken, the regression results are printed at each step of the analysis or at its completion. The following items are listed for each variable included in the regression: Variable identification and label, regression coefficient, F-ratio and beta weight (coefficient).

9. The program then asks if the residual summary is desired. If the answer is "YES", the following results are printed for each observation: The observed Y-value, the calculated Y-value, the residual or error, the percent error, and the cumulative sum of the squared errors (C-ER 2).

10. The user is then asked to indicate which one of the following actions the program is to take: (1) request a new data file, (2) select a new set of variables from the current data file, (3) alter the critical F-value or confidence level, (4) terminate program execution.

SAMPLE PROBLEM

A listing of the data and program output for a sample regression problem is shown on the following pages. The sample problem contains 16 observations of 11 variables. The transformation coding does nothing constructive and is included only for the purpose of illustration. The regression analysis was run using variable 10 as the dependent variable and variables 1 - 9 as the independent variables. Variable 9 was forced into the regression. The confidence level was entered as 0.90.

The regression results show that 90.35% of the total variation in the dependent variable was explained by variables 1, 2, 3, 5, and 9. Looking at variable 9, it is apparent that there was no need to force this variable into the regression. The F-ratio of 9 was 9.92, well above the critical F-value of 3.29. The remaining unexplained variation (RSS) was 43.60 and the estimate of the error about the regression line was 2.09. Variables 4, 6, 7, and 8 were not significant at the 0.90 confidence level.

When the critical F-value was reduced to 0.1, all the independent variables were included in the regression. R^2 increased from 0.904 to 0.959, while the standard error of the estimate decreased from 2.09 to 1.77. From inspecting the F-ratios, it is apparent that variables 6 and 8 contributed very little to the overall fit.

As an interesting exercise, the user is urged to run this same problem, including all the independent variables in the regression by using a critical F-value of 0.1. After the results have been printed, enter a confidence level of 0.90. The final results will be different from those obtained by initially entering a confidence level of 0.90. In fact, two more significant variables will be included in the results. Although the sample data is "manufactured", this situation does occur with real live data and points out that backward deletion of variables is sometimes better than forward addition.

```
*LIST LØDAT

11
TRNF   11
CØN  21 -10.25 1
MPY  11 21 23
DVD 23 21 23
MØV  23 11 1
END  1 1 1
LABL 11
XV1 XV2 XV3 XV4 XV5 XV6 XV7 XV8 XV9 YV10 YV11 ELAB
-1 -1 -1 1 1 1 1 1 1 52.5 6.12
1 -1 -1 1 1 1 -1 -1 1 44.4 9.54
-1 1 -1 1 1 1 -1 1 -1 40.6 8.32
1 1 -1 1 1 1 1 -1 -1 36.0 9.88
-1 -1 1 1 1 1 1 -1 -1 43.0 13.31
1 -1 1 1 1 1 -1 1 -1 36.0 16.52
-1 1 1 1 1 1 -1 -1 1 39.3 9.97
1 1 1 1 1 1 1 1 1 38.0 11.17
0 0 0 0 0 0 0 0 0 38.0 12.58
0 0 0 0 0 0 0 0 0 37.4 12.22
2 0 0 4 0 0 0 0 0 35.5 13.76
-2 0 0 4 0 0 0 0 0 46.6 12.37
0 2 0 0 4 0 0 0 0 37.5 9.21
0 -2 0 0 4 0 0 0 0 52.6 9.67
0 0 2 0 0 4 0 0 0 37.9 13.19
0 0 -2 0 0 4 0 0 0 39.5 5.57

READY


*RUN
STEPWISE MULTIPLE LINEAR REGRESSIØN PRØGRAM


ENTER DATA FILE 'NAME'
= LØDAT
 11 INITIAL VARIABLES
 11 TRANSFØRMED VARIABLES
 16 ØBSERVATIØNS
MEANS
= YES

VAR  LABEL          MEAN      STD-DEV         MIN           MAX
  1    XV1        0.          1.0328  -2.0000E+00   2.0000E+00
  2    XV2        0.          1.0328  -2.0000E+00   2.0000E+00
  3    XV3        0.          1.0328  -2.0000E+00   2.0000E+00
  4    XV4        1.0000      1.2649   0.           4.0000E+00
  5    XV5        1.0000      1.2649   0.           4.0000E+00
  6    XV6        1.0000      1.2649   0.           4.0000E+00
  7    XV7        0.          0.7303  -1.0000E+00   1.0000E+00
  8    XV8        0.          0.7303  -1.0000E+00   1.0000E+00
  9    XV9        0.          0.7303  -1.0000E+00   1.0000E+00
 10    YV10      40.9250      5.4894   3.5500E+01   5.2600E+01
 11    YV11      10.8375      2.8704   5.5700E+00   1.6520E+01
CØRR. MATRIX
= YES
```

```
CØRRELATIØN MATRIX

        [  1]    [  2]    [  3]    [  4]    [  5]    [  6]    [  7]    [  8]
   [  9]    [ 10]    [ 11]
[  1]
        1.000
[  2]
        0.       1.000
[  3]
        0.       0.       1.000
[  4]
        0.       0.       0.       1.000
[  5]
        0.       0.       0.      -0.333    1.000
[  6]
        0.       0.       0.      -0.333   -0.333    1.000
[  7]
        0.       0.       0.       0.       0.       0.       1.000
[  8]
        0.       0.       0.       0.       0.       0.       0.       1.000
[  9]
        0.       0.       0.       0.       0.       0.       0.       0.
        1.000
[10]
       -0.508   -0.614   -0.240    0.033    0.340   -0.148    0.153    0.073
        0.309    1.000
[11]
        0.274   -0.159    0.727    0.293   -0.240   -0.248   -0.123   -0.018


       -0.357   -0.426    1.000
ENTER NØ. ØF 'X' VARS, THEN INDEX ØF 'Y' VAR
FØLLØWED BY INDICES ØF ALL 'X' VARS
= 9,10,-9,1,2,3,4,5,6,7,8
ENTER F ØR CL FØR: CRITICAL F-VALUE ØR CØNFIDENCE LEVEL
= CL
ENTER CØNFIDENCE LEVEL
= 0.90
STEPWISE RESULTS?
= NØ

LQDAT    : 1   DEP-VAR=10:  YV10  CL=0.90  DØF= 15  RSS=       45
.0100                               2

STEP    VAR:LABEL      F-CRIT    DØF      R-SQ          SEE
  1     * 9:  XV9       3.10     14     0.0957        5.4035
  2     + 2:  XV2       3.14     13     0.4724        4.2829
  3     + 1:  XV1       3.18     12     0.7305        3.1862
  4     + 5:  XV5       3.23     11     0.8460        2.5155
  5     + 3:  XV3       3.29     10     0.9035        2.0880

VAR  LABEL         CØEFFICIENT        STD-ERR      F-RATIØ        BETA-WT
  1    XV1           -2.700000         0.5220        26.75        -0.5080
  2    XV2           -3.262500         0.5220        39.06        -0.6138
  3    XV3           -1.275000         0.5220         5.97        -0.2399
  5    XV5            1.475000         0.4262        11.98         0.3399
  9    XV9            2.325000         0.7382         9.92         0.3093
CØNS                 39.449998
```

```
LODAT   : 1  DEP-VAR=10:  YV10  CL=0.90  DOF= 10  RSS=        43.5975

RESIDUALS?
= NO
ENTER A 1,2,3 OR 4FOR:  1-SELECT NEW DATA FILE
2-SELECT NEW VARIABLES, 3-SELECT NEW 'F' OR 'CL',
4-END OF RUN
= 3
ENTER F OR CL
= F
ENTER CRITICAL-F
= 0.01
STEPWISE RESULTS?
= NO

LODAT   : 2  DEP-VAR=10:  YV10  CL=0.     DOF= 10  RSS=        43.5975

STEP    VAR:LABEL      F-CRIT    DOF       R-SQ          SEE
  6     + 4:  XV4       0.01      9      0.9275       1.9081
  7     + 7:  XV7       0.01      8      0.9509       1.6654
  8     + 8:  XV8       0.01      7      0.9563       1.6805
  9     + 6:  XV6       0.01      6      0.9585       1.7686


VAR  LABEL          COEFFICIENT         STD-ERR      F-RATIO         BETA-WT
  1     XV1            -2.700000         0.4421        37.29         -0.5080
  2     XV2            -3.262500         0.4421        54.45         -0.6138
  3     XV3            -1.275000         0.4421         8.32         -0.2399
  4     XV4             0.837500         0.4421         3.59          0.1930
  5     XV5             1.837500         0.4421        17.27          0.4234
  6     XV6             0.250000         0.4421         0.32          0.0576
  7     XV7             1.150000         0.6253         3.38          0.1530
  8     XV8             0.550000         0.6253         0.77          0.0732


  9     XV9             2.325000         0.6253        13.83          0.3093
CONS                   37.999999

LODAT   : 2  DEP-VAR=10:  YV10  CL=0.     DOF=  6  RSS=        18.7675

RESIDUALS?
= YES

OBS        Y-OBS        Y-CALC          ERROR       %-ERR        C-ER↑2
  1       52.5000       52.1875         0.3125       0.60        0.0977
  2       44.4000       43.3875         1.0125       2.33        1.1228
  3       40.6000       38.7125         1.8875       4.88        4.6855
  4       36.0000       34.5125         1.4875       4.31        6.8982
  5       43.0000       43.8875        -0.8875      -2.02        7.6858
  6       36.0000       37.2875        -1.2875      -3.45        9.3435
  7       39.3000       39.7125        -0.4125      -1.04        9.5136
  8       38.0000       37.7125         0.2875       0.76        9.5963
  9       38.0000       38.0000         0.0000       0.00        9.5963

 10       37.4000       38.0000        -0.6000      -1.58        9.9563
 11       35.5000       35.9500        -0.4500      -1.25       10.1588
 12       46.6000       46.7500        -0.1500      -0.32       10.1813
 13       37.5000       38.8250        -1.3250      -3.41       11.9369
 14       52.6000       51.8750         0.7250       1.40       12.4625
 15       37.9000       36.4500         1.4500       3.98       14.5650
 16       39.5000     . 41.5500        -2.0500      -4.93       18.7675
ENTER A 1,2,3 OR 4
= 4

PROGRAM STOP AT 4040
*
```