DEDICATION

DEDICATED TO HIM
THE ANCIENT OF DAYS
IN WHOM ALL THINGS RESIDE
AND BY WHOM ALL THINGS CONSIST
WHO HEREUNTO HAD HELPED ME
WHO REDEEMED MY LIFE
AND GAVE ME PEACE AND PURPOSE
PLUS THE JOY OF LIVING
IN THIS OTHERWISE CHAOTIC WORLD
TO HIM ALONE BE THE HONOUR

PVC STABILISERS BASED ON METAL CARBOXYLATES

by

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JACOB BOYE ADENIYI : Ph.D : 1984

SUMMARY

Hydroperoxides and olefinic unsaturation are formed rapidly in Polyvinyl chloride (PVC) as a consequence of mechanical shearing of the polymer chains during the processing operation. The concentration of these species in the polymer before processing is negligible compared with that produced mechano-chemically during processing. It is considered that shearing of PVC during processing is the main source of chemical impurities in the polymer which lead to instability during subsequent service.

Wax E, a commercial ester lubricant and Calcium stearate were found to reduce the severity of the mechano-chemical damage to the polymer during processing and the formation of unsaturation and peroxides was delayed by Dibutyltin maleate (DBTM), a commercial stabiliser which not only reacts with allylic chlorine and hydrogen chloride but also undergoes Diels Alder addition to conjugated unsaturation. Lead stearate also reduced colour formation in PVC during processing but was less effective than DBTM during subsequent thermal and photo-oxidative degradation.

Hydroperoxides in association with unsaturation formed during processing functioned as photo-initiators during subsequent ultraviolet irradiation and DBTM which effectively retarded the formation of these species during processing exhibited photo-stabilising activity. Under thermal oxidative conditions, the stabilising effect of DBTM was substantially improved by commercial phenolic antioxidants: Irganox 1300, 1076 and 1010 although these reduced slightly the induction period to colour formation during processing particularly at low concentrations of DBTM.

The photo-oxidative stability of PVC stabilised with DBTM was synergistically improved by 2-Hydroxyl-4-octoxybensophenone (UV531), Bis (2,2,6,6-tetramethyl piperidine) sebacate (Tinuvin 770) and its derived bisnitroxyl, and to a leser extent by 4-Hydroxyl-2,2,6,6 - tetramethyl piperidine and its derived nitroxyl radical and hydroxylamine. 1,3- Dihydroxyl-2- hydroxylmethyl-2-nitro propane (Tris Nitro) and 1,3 - Dihydroxyl-2-hydroxylmethyl-2- amino propoane (Tris Amine) and esters of the nitro compound all functioned as photostabilisers but they were less efficient than Tinuvin 770

The mechanisms of degradation of PVC and its stabilisation are discussed.

KEY WORDS: POLYVINYLCHLORIDE, UNSATURATION, PEROXIDES, DEGRADATION, STABILIZATION.

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DECLARATION

The work described herein was carried out at the University of Aston in Birmingham between October 1981 and July 1984.

It has been done independently and submitted for no other degree.

July 1984

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INTRODUCTION

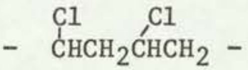
In terms of worldwide commercial significance, polyvinyl chloride (PVC) outranks every other class or family of polymers both in diversity of applications and in the total volume of finished product output. This fact derives, to a large extent, from the great variety of processes in which PVC can be fabricated and of the forms in which they can appear in the final products coupled with the fact that PVC compositions generally contain large amounts of modifying agents such as plasticisers, fillers, impact modifiers, stabilisers and so on. Polyvinyl chloride products have found extensive applications in building and construction, apparel, electrical and electronic industries, automobile, home furnishings, packaging, recreation, transportation, agriculture, and in other miscellaneous articles.

The stabilisation of PVC against the effects of heat and light still remains the most pressing problem connected with this polymer. Hydrogen chloride (HCl) was the first product of PVC degradation to be recognised. It was known to be troublesome not only due to its odour and corrosive action, but because in some way, the degradation became worse as more free acid formed. It was for this reason that the stabilising value of substances forming insoluble chlorides was recognised for their ability to remove free HCl, leading to better thermal stability of the polymer. Hydrogen chloride acceptors, of which basic lead carbonate is the most important, were the first PVC stabilisers. Advances in PVC stabilisation to this level were purely empirical.

The first attempts to study systematically what happens when PVC degrades marked the end of the belief that hydrogen chloride catalysis was the sole significant factor in the dehydrochlorination process. Boyer[1], in 1947, reported the presence of carbonyl groups in degraded PVC, showing that oxygen was also involved in the reaction. Fox and co-workers[2] also demonstrated the formation of polyene systems and conjugated carbonyl groups in degraded PVC. Boyer[1] explained the existence of these groups in PVC and also established a relationship between the changes in colour of PVC due to thermal action and the polyene structure resulting from the loss of HCl.

1.1 Effect of Structure on PVC Stability

Experimental evidence [3-5] shows that the regular 1,3-dichloride structure (I) is the main component of PVC. This structure should be stable to temperatures much higher than those at which PVC is found to degrade.[6-10] Low molecular weight model compounds analogous to (I)



$$-\overset{\text{Cl}}{\text{C}}\text{HCH}_2\overset{\text{Cl}}{\text{C}}\text{HCH}_2-$$

I

are known to be stable at 300°C [11-13] whereas PVC degrades when heated at 100°C[14,15] with concomitant HCl evolution and discolouration. The presence of structural imperfections has been suggested to be responsible for the relative instability of PVC compared with the low molecular weight alkylhalides.[6,16,17] Structural abnormalities could arise by a variety of processes including chain ends attached to initiator fragments [16,17], unsaturated end groups[16-18] resulting from chain transfer to monomer during polymerisation [6,10], oxidation products, branching sites and tertiary chlorides in addition to extraneous impurities.

Allylic and tertiary chlorides have been implicated as the unstable sites which initiate dehydrochlorination[6-10,19,20] and the displacement of allylic chloride was found to improve the stability of PVC[6,20-24]. It has also been suggested that the presence of less than 0.2 mole % of tertiary chlorides could account for the instability of PVC[25]. Baum and Wartman[19] also demonstrated that hydrogen chloride loss in PVC may be initiated from terminal unsaturation. It is known[26] that unsaturated compounds are particularly prone to peroxidation and it was shown that minor amounts of initial unsaturation is a major cause of subsequent degradation due to allylic hydroperoxide formation[27-30]. Peroxides have been reported[31] in virgin PVC and the low activation energy required for homolysis of 0-0 bond[32] permits these species to act as probable initiators for dehydrochlorination of PVC.

It must be emphasised here that the unsaturation produced during the processing operation (mechanochemical degradation) completely swamps whatever irregularity might be present in the polymer after manufacture. Consequently, most of the academic studies on the nature of structural defects in virgin PVC and their effects on its degradation have little practical relevance to the technological conditions to which PVC is subjected during fabrication e.g. in an industrial screw extruder or laboratory mixer. Therefore, the processing operation (or thermal history, as it is occasionally referred to) affects the stability and service life of PVC more than any other factor. This is so because, not only does mechanodegradation increase the rate of the oxidation process and the introduction of a variety of irregularities into the macromolecule, but it also affects the rate of consumption and transformation of antioxidants incorporated into PVC formulations.

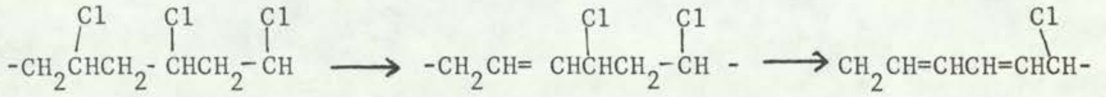
1.2 Degradation of PVC

The two most immediate effects of thermal degradation of PVC are the liberation of HCl and the noticeable discolouration of the degraded polymer. Subsequently, the less-evident influence of oxygen attack becomes apparent. The nature of the product was indicated by Marvel et al[4] who showed that the degraded polymer exhibits reactions typical of unsaturated hydrocarbons. A polyene structure with conjugated double bonds is generally accepted as the degraded product. Colour, which is indisputably perceptible in degraded PVC arises from the conjugated double bonds; the latter species are prone to oxidation and disruption in an atmosphere of oxygen.

The thermal degradation of PVC in an anaerobic (nitrogen) atmosphere proceeds at a constant rate and is independent of the ambient concentration of hydrogen chloride[15], demonstrating that the dehydrochlorination is not autocatalytic. Crosslinking reactions predominate under these conditions arising probably from reactions between unsaturated portions of the polymer chain. Crosslinking is accompanied by insolubility, associated with molecular weight increase of the polymer. The constant rate of dehydrochlorination of PVC in an inert atmosphere is replaced by an accelerated evolution of HCl in an oxygen (aerobic) atmosphere.[15,33-35] It is evident therefore that oxidation plays an active part in the degradation process. Oxygen is capable of increasing the concentration of dehydrochlorination initiators by the formation of hydroperoxides at labile sites such as unsaturated chain ends or polyene sequences in degraded polymer chains. Polymer chain scission with accompanying reduction in molecular weight is observed in an oxygen atmosphere as opposed to crosslinking in an inert atmosphere.[15,32] Chain scission reactions in the presence of oxygen may be associated with kinetic chain transfer processes involving thermolysis of hydroperoxides into alkoxyl radicals and the further transformation of the derived alkoxyl species into carbonyl compounds.[32,36]

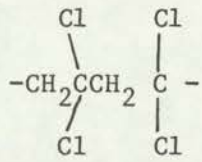
Similar results are obtained in anaerobic photodegradation of PVC as in thermal degradation under the same conditions[32.37]. However, whereas heat causes a strong discolouration together with a minor loss of mechanical properties, light on the other hand, causes little discolouration but a distinct decrease in elongation, loss in flexibility, and increase in brittleness[37]. In an atmosphere of nitrogen or under vacuum, photodegradation causes an increase in molecular weight indicative of crosslinking. The formation of HCl is more rapid in the presence of oxygen than in an inert atmosphere and samples which were strongly discoloured as a result of thermal degradation lost their colour when subjected to the further action of light in oxygen[37]. In addition to the bleaching of the colour of degraded PVC, oxygen causes chain scission with associated reduction in molecular weight[38]. Oxidation is opposed, in part, to the discolouration of samples probably via saturation of double bonds formed by dehydrochlorination. The unsaturated structure produced by HCl elimination facilitates both the attack of oxygen with subsequent carbonyl group formation and the creation of crosslinkages. However, since oxidation plays a predominant role, the formation of crosslinkages is diminished in relation to those which are formed in an inert atmosphere.

To account for polyene formation under anaerobic degradation, directed HCl elimination has been postulated by Marvel et al[3-5] in which the elimination of the chlorine atom α to the conjugated system is favoured (1).

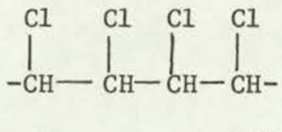


$$-CH_2\overset{Cl}{C}HCH_2-\overset{Cl}{C}HCH_2-\overset{Cl}{C}H \longrightarrow -CH_2CH=CH\overset{Cl}{C}HCH_2-\overset{Cl}{C}H- \longrightarrow CH_2CH=CHCH=CH\overset{Cl}{C}H- \quad (1)$$

It was shown[33] that when PVC is chlorinated, methylene hydrogens disappear. The major portion of the product does not have the polyvinylidine chloride structure II, but one chlorine atom is attached to each carbon atom, III. This indicates that the major portion of free radical attack is on the methylene hydrogen atom. Fuchs and Louis[39] also demonstrated that radical attack occurs on a methylene hydrogen atom preferentially. This produces a labile chlorine atom in a β-position which is then released to stabilise the structure. The newly formed chlorine atom abstracts a proton from another methylene group, thereby in turn producing the next labile chlorine atom. Hence, a chain reaction is initiated and propagated, leading to conjugated structures; such structures with sufficient number of double bonds should be coloured.



II



$$-\overset{\mathrm{Cl}}{\mathrm{CH}}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\overset{\mathrm{Cl}}{\mathrm{CH}}-\overset{\mathrm{Cl}}{\mathrm{CH}}-$$

III

1.2.1 Catalytic Effect of Hydrogen Chloride

Much controversy has centred around the role of HCl liberated during the early stage of degradation on the subsequent dehydrochlorination of PVC. While some authors reported catalytic acceleration by HCl,[6-10] others retardation,[40] yet others have claimed that HCl has no effect in the absence of oxygen[15,33,41,42] or light.[33,43] It is known that the presence of traces of metals in an autoxidising system results in a more rapid rate of chain initiation than in their absence.[44]

It seems possible then that HCl is deleterious because it can attack and solubilise metals, such as iron, with which the PVC comes in contact during fabrication. For example, Baum[45] demonstrated that ferric chloride is an effective catalyst both for HCl evolution and for the associated discolouration.

Recent reports by Cooray and Scott[46,47] show that the mechanism of the catalytic decomposition of peroxides by HCl involves competing ionic and free radical redox processes and that the molar availabilities of the peroxide and HCl play a significant role in the observed effect of HCl on the rate of dehydrochlorination. An equilibrium between radical generating and ionic peroxide decomposition processes is found to occur at an equimolar ratio of hydroperoxide to hydrogen chloride. At higher ratios, ionic decomposition predominates while at lower values, free radical decomposition is fovoured. This indicates that a sub-molar proportion of HCl to hydroperoxide could have a positive stabilising effect whereas supramolar quantities will lead to radical initiation. The well known catalytic effect of HCl on PVC degradation may possibly be caused by the catalytic free radical redox decomposition of trace quantities of peroxides by HCl leading to increased radical initiation of hydrogen chloride elimination in the polymner matrix. This behaviour of HCl is akin to many acidic organic compounds which are known to have a dual capability of destroying hydroperoxides by ionic processes and by redox radical generating reactions. Typical examples of such compounds are the sulphinic and phosphorus acids, which in combination with hydroperoxides are either pro-oxidants or antioxidants depending on the molar ratio of hydroperoxides to sulphur or phosphorus acid respectively.[48-51]

Unequivocally, the above results of Cooray and Scott[46,47] explain to a large extent the controversy and conflicting reports on the effect of HCl on the subsequent dehydrochlorination of PVC. It appears therefore that the main factor underlying the differences in other reports cited is probably the oxygen content in the media of degradation and/or more specifically, the hydroperoxide concentration in the polymer samples.

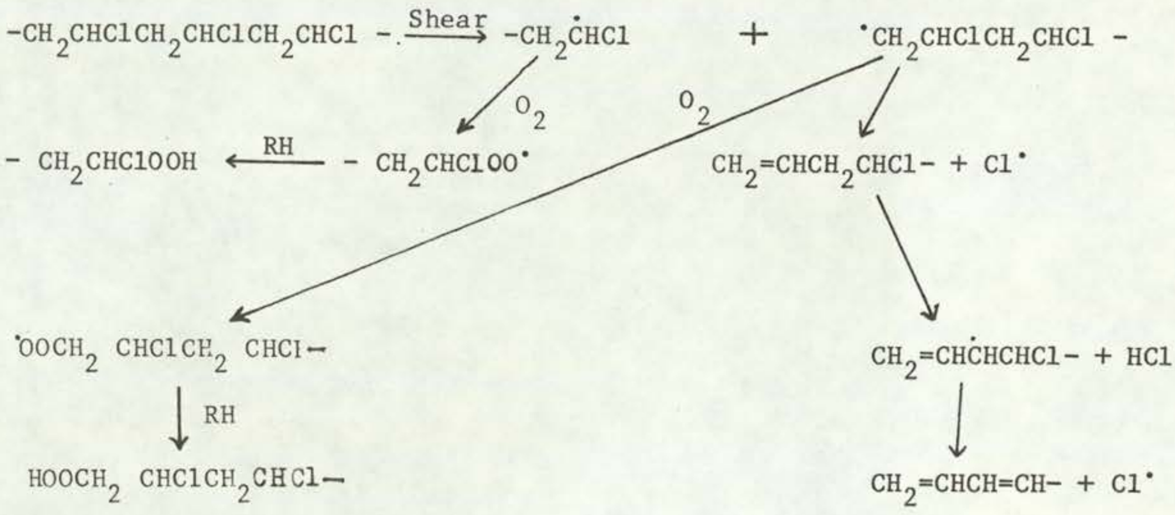
1.2.2 Effect of Thermal Processing

Plastics and rubbers are both subjected to mechano-oxidation during thermal processing and conversion processes. The industrial procedures used in the conversion of polymers to finished products almost always involve the use of a screw extruder to homogenise and convey the molten polymer. This can be a serious problem in the case of plastics and necessitates the use of melt stabilisers in some cases.[52] Mechanodegradation arising from the powerful shearing forces to which the polymer is subjected in an industrial screw extruder or laboratory mixer leads to chain scission and macroalkyl formation. The effect of this is to increase the rate of the oxidation process and the rate of consumption of antioxidants. Since a small amount of oxygen is always present either dissolved in the polymer or trapped in the polymer feed, an important practical consequence of mechanochemical degradation is the introduction of oxygen-containing functional groups which profoundly affect the service performance of the polymer.

It is important, both theoretically and practically, to know what effect the processing operation has on the polymer and the subsequent performance of antioxidants and stabilisers in polymers. That antioxidants and stabilisers are affected by processing is self-evident in the light of the chemical changes known to occur in polymers under these conditions[53,54]. Recent studies have shown[28-30,53,54] that all thermoplastic polymers show a high rate of mechanodegradation in the initial stages of processing operation, leading to the introduction of a variety of irregularities into the macro-molecule. The easiest of these to measure are carbonyl compounds, hydroperoxides and unsaturation[28-46]. These impurities have been shown to have a profound effect, not only on the subsequent ageing performance of the unstabilised polymer but also on the antioxidants and stabilisers incorporated during processing. This may result either in the partial destruction of the effective antioxidant species or in its formation from an inert precursor.

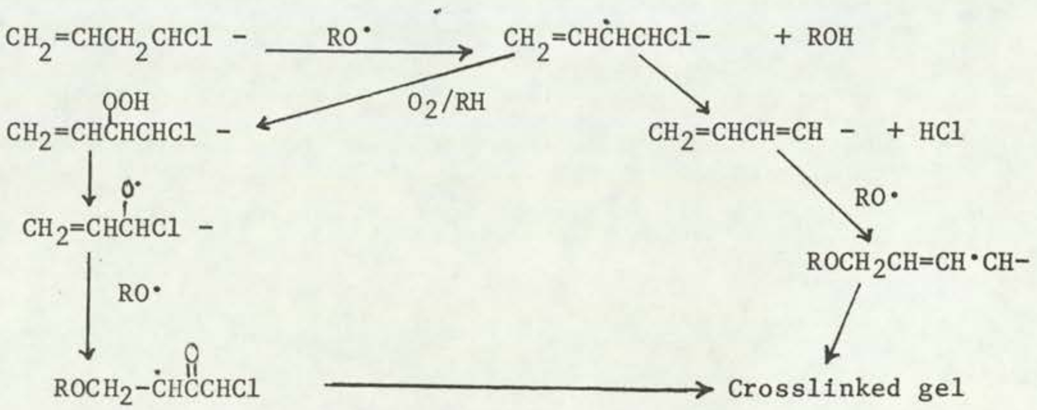
Mechanochemical chain scission is readily observed in PVC[29]. Scheme 1 outlines the chemical reactions which have been shown to occur. Most of the damage to the polymer occurs during the first minute of processing when the viscosity of the polymer is high. Similar reactions occur during the processing of most polymers[54-58] but the damage inflicted on the polyolefins is less visually obvious than it is in the case of PVC which discolours badly due to the formation of polyconjugation in the polymer chain. Hydroperoxide groups formed by reaction of oxygen with the macroalkyl radicals are also potent sensitisers for thermal and photo-oxidative degradation both during processing and in subsequent service[28-30,55]

Scheme 1: Mechanochemical formation of unsaturation and peroxides in PVC



The chemistry subsequent to the initial mechanochemical chain scission of the polymer has been interpreted in terms of competition between the reaction of the initially formed radical with oxygen and elimination of a chlorine atom to form a vinyl end group. The subsequent thermal degradation reactions lead to the formation of conjugated unsaturation with associated colour, further peroxides, and crosslinked gel in the polymer. The allylic groups formed in the mechanochemical stage are intimately involved in all these processes (scheme 2)[54]

Scheme 2: Gel formation during mechanodegradation of PVC



It may be concluded that mechanochemical shearing under conditions of heat, which is characteristic of the processing of PVC at elevated temperatures and in the presence of unavoidable amount of oxygen, inflicts more damage on PVC than any other process.

It has been demonstrated that the rate of photo-oxidation of unstabilised PVC is markedly dependent on the severity of the processing operation^{30} and that thermally produced peroxides in combination with unsaturation constitutes a powerful photo initiating system^{57}.

Therefore the processing operation profoundly affects the thermal and photo-oxidative stability of PVC.

1.2.3 Effects of Metal Ions

The pro-oxidant effects of metal ions capable of undergoing one-electron redox reaction are well documented. Evidence suggests that metal ions exert their catalytic effect upon autoxidation by forming unstable coordination complexes with alkyl hydroperoxides, followed by electron transfer to give free radicals[44,59]. Two types of redox reactions can be involved depending on the metal ion and its state of oxidation (2,3). A strong reducing agent such as ferrous ion reacts

$$ROOH + M^{n+} \longrightarrow M^{(n+1)+} + RO^{\cdot} + HO^{-} \qquad (2)$$

$$ROOH + M^{(n+1)+} \longrightarrow M^{n+} + ROO^{\cdot} + H^{+} \qquad (3)$$

according to equation (2) to form alkoxyl radicals whereas a strong oxidising agent such as lead tetraacetate reacts with hydroperoxide to form alkylperoxyl radicals, $ROO^{\cdot}$, as in equation (3). When the metal ion has valence states of comparable stability eg. Co^{2+} and Co^{3+}, both reactions will occur and a trace amount of the metal can convert a large amount of hydroperoxides to free radicals according to the sum of the two reactions (4).

$$2\ ROOH \xrightarrow{Co^{2+}/Co^{3+}} RO\cdot + ROO\cdot + H_2O \qquad (4)$$

The effect of the metal ion is thus to speed up the rate of initiation by accelerating the rate of peroxide decomposition to free radicals through the lowering of the activation energy of the peroxide decomposition by catalysis (4). Reaction (4) is of extreme importance in the catalysis of autoxidation because of the minute quantities of metal ions (e.g. iron [33,45]) which can be effective. Transition metal impurities even at very low concentrations have been found to affect the stability of PVC. Arlman[33] found that 10 ppm iron had little effect in a nitrogen atmosphere but increases dehydrochlorination by

30% in oxygen. Ferric chloride has also been shown to catalyse dehydrochlorination[35]. Certain metal chlorides formed during degradation by reaction of HCl with stabilisers may also catalyse dehydrochlorination at concentrations in excess of 2 x 10^{-3} mol/l[60]. Metal salts, particularly Lewis acid species $FeCl_3$, $ZnCl_2$ and $CdCl_2$ have been postulated to function as active catalysts for further dehydrochlorination causing autocatalysis[10].

1.3 Stabilisation of PVC

Polyvinyl chloride is prone to degradation during processing under shear and in service under the influence of light, high temperatures and oxygen the main manifestations of degradation are: evolution of hydrogen chloride, discolouration, deterioration of mechanical properties and chemical modifications of the polymer chain-particularly chain scission and crosslinking and the formation of carbonyl and hydroxyl species. The prevention of any or all of the degradative reactions by the addition of chemicals (generally referred to as stabilisers) to the compounded polymer is known as stabilisation. As the name implies the object is to stabilise the polymer against the deleterious effects of degradation. Stabilisers are therefore incorporated into PVC formulations for protection against degradation under the influence of heat and mechanical shear during processing, and also to afford long-term protection in service, mainly against the effects of light, heat and oxidation.

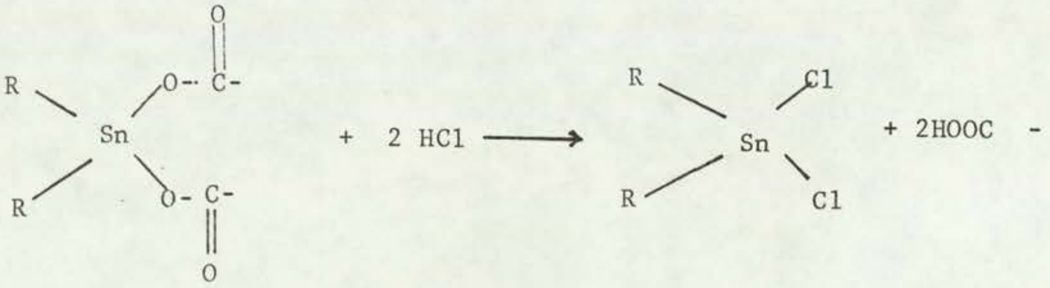
The mechanism of PVC stabilisation is rather complex and not fully elucidated yet in spite of continuous research into this subject. To a large extent PVC stabilisation technology is still an empirical process.

The common features of commercial PVC stabilisers are their ability to react with HCl thus alleviating harmful hydrogen chloride catalysis. The stabilising properties of organotin derivatives for example, derive from one or more of the following: capacity for HCl absorption, ability to replace labile chlorine in the polymer to give a more thermally stable group, ability to react with unsaturation, ability to destroy hydroperoxides and the possibility of disrupting free radical chain processes. According to Scott[44], PVC stabilisers may be summarised into at least six mechanistic types: (1) conventional chain breaking antioxidants; (2) hydrogen chloride scavengers, (3) labile chlorine reagents; (4) non-radical hydroperoxide decomposers; (5) uv absorbers and (6) enophilic reagents.

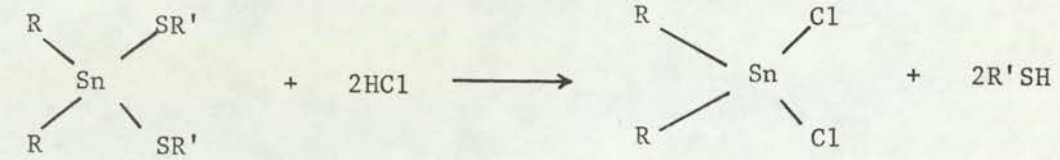
1.3.1 **Stabilisation by Hydrogen Chloride Scavengers**

A wide variety of PVC stabilisers have been reported to function by removing or neutralising HCl[6,22]. Dialkyltin carboxylates and mercaptides are known to react with HCl by a rapid stoichiometric process. Dialkyltin dichlorides which are the reaction products, have been shown to be ineffective in catalysing dehydrochlorination[10,21,61].

For carboxylates and mercaptides, the reactions involved are as shown in reactions (5) and (6) respectively.



(5)



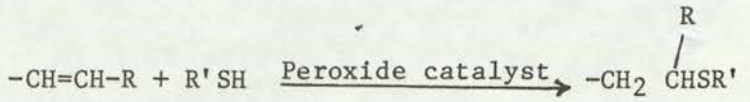
(6)

Metal soaps of zinc, cadmium, barium, calcium, strontium and magnessium have also been reported to be involved in similar stoichiometric reactions with HCl. As individual compounds, the dialkyltins are by far the most widely used and effective stabilisers, however, much recent work has been directed to developing synergistic mixtures of dialkyl and monoalkyltins which are said to give improved performance[62-64]. In general the mercapto-acetates (thioglycolates) or mercapto-propionates give by far the best thermal stability but confer little subsequent photo-stability[65]. Of the sulphur-free stabilisers, the various maleate ester compounds are probably the best and in addition may give a measure of photo-stability[66]. Organotin compounds are generally highly efficient thermal stabilisers and in this role they may well improve photo-stability by preventing or minimising the formation of photo-sensitizing chromophores. However, some organotins actually promote photo-degradation[65,67].

1.3.2 Stabilisation by Labile Chloride Reagents

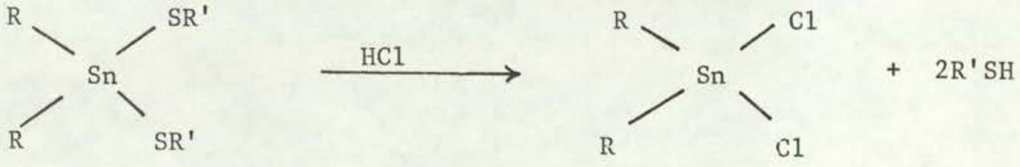
Frye, Horst and Paliobagis [21,68] showed that the reaction of metal carboxylates with PVC during thermal ageing leads to the incorporation of ester groups of the stabilisers into the polymer. The stabilising effectiveness of organotin and other metal soaps have therefore been explained in terms of replacement of labile chloride by ester groups with consequent increase in the stability of the polymer. This observation has been fully substantiated by subsequent work.[24,27] The original hypothesis involving formation of co-ordination complexes between chlorine attached to the polymer and tin atoms in stabilisers[21] has not gained much support[6] but there is abundant evidence that allylic chlorine atoms are replaced by substituent groups from the stabiliser [24,27,65] with confirmatory evidence that removal of labile halogen results in greatly improved thermal stability[24].

Starnes[24,69] demonstrated that chemical stabilisation results from pretreatment of PVC with organotin mercaptides and that the magnitude of the effect can be correlated with the number of chemically bonded mercaptide moieties[70-72]. Thiol addition to monounsaturation in PVC stabilised with dioctyltin bis(isooctyl thioglycollate) has been reported by Cooray and Scott[67]. The decrease in the initial unsaturation formed in the polymer as a consequence of mechano-chemically induced dehydrochlorination was suggested to indicate that thioglycollic ester rapidly adds to non-conjugated double bonds (7) in the presence of hydroperoxides which are other products of the reaction during the early stages of processing.[27-30] Dialkyltin thioglycolates, like the



$$-CH{=}CH{-}R + R'SH \xrightarrow{\text{Peroxide catalyst}} -CH_2\overset{R}{C}HSR' \qquad (7)$$

dialkyltin maleates, have been shown previously[70] to react with both allylic chlorine and with hydrogen chloride. The latter process gives rise to the corresponding thioglycollic ester (8), which in turn has been implicated in reaction (7)[67]



(8)

1.3.3 Stabilisation by Enophilic Reagents

Baum and Wartman[19] suggested that the terminal double bonds in PVC are largely responsible for the labilisation of the active chlorine atoms. Consequently, chlorination of residual unsaturation was found to significantly reduce the rate of dehydrochlorination. These reports are related mostly to unprocessed virgin PVC and the more important role of mechanical processing had not received the attention it deserves until quite recently. Whatever the arguments may be about the thermal stability of a perfect PVC structure or whatever imperfections may arise during polymerisation, there can be no doubt that mechanical working on an industrial roll mill or laboratory Banbury mixer or similar machines, in air at high temperatures, will fracture polymer molecules and reintroduce unsaturation and other reactive species into the polymer. The relevance of the inherent defects in the structure of the virgin polymer after manufacture to the stability of PVC under technological conditions employed to fabricate this polymer into its products is therefore questionable.

Scott and co-workers[27-30] have shown that when unstabilised PVC is processed to 170-210°C, it undergoes immediate mechano-chemically induced thermal oxidation with the formation of unsaturation and peroxides and these sensitise the polymer to subsequent thermal and photo-oxidative degradation. A dialkyltin thioglycolate stabiliser was found to reduce the initially formed olefinic unsaturation by thiol addition (7), whereas a commercial dibutyltin maleate stabiliser does not.[67] The tin maleate stabiliser however reacts with conjugated double bonds formed subsequently by a Diels-Alder reaction and in this case the unsaturation remains constant until the stabiliser is depleted in the polymer[27]. Compounds capable of undergoing Diels-Alder reaction with conjugated bonds e.g. maleic and fumaric acids and their derivatives and tin salts of maleic acid have been commonly used to reduce colour formation in PVC. The mechanism of stabilisation by thiol addition not only involves the removal of initial unsaturation (non-conjugated) but also effectively introduces stable groups into the polymer backbone and as such, under processing conditions, the formation of conjugated unsaturation by a secondary process would be substantially delayed. Organotin mercaptides have also been found to improve the colour of PVC which was subjected to a preliminary thermal treatment[66]. This effect may perhaps be attributed in part to an efficient bisection of the polyene structures by thiol addition.

Since discolouration is a major problem in PVC particularly under processing conditions, it is beneficial to devise synergistic melt stabilisers capable of reacting with both the initial saturation (non-conjugated) and the subsequent conjugated double bonds.

1.3.4 Stabilisation by Peroxide Decomposers

Hydroperoxides homolyse readily under the influence of light[73] and heat[44] and produce alkoxyl and alkylperoxyl radicals under the influence of metal ion catalysis[44] Agents which remove hydroperoxides in a non-radical mechanism or which protect hydroperoxides from decomposition should therefore in principle, effectively inhibit oxidation[74]. Antioxidants which destroy hydroperoxides either stoichiometrically as with phosphite esters [51,75] or catalytically as with thiols, monosulphides and disulphides[44,48-50,76] effectively inhibit peroxide accumulation during processing and oxidative degradation of polymers.

It has been known for many years that sulphur compounds are effective synergistic stabilisers for PVC[44] and although peroxide decomposition has been suggested as one possible method by which they may function [46,47,70] there was until recently little evidence to suggest that hydroperoxides play a significant part in the thermal degradation of PVC. Studies in model systems have however led to the recognition of the great importance of redox reactions between hydroperoxides and HCl during technological processing operations [46,47,77] and in this situation, sulphur compounds might be expected to play a part both during processing and during subsequent ageing.[46,47,65]. Dialkyltin thioglycollates are particularly effective under conditions of thermal oxidation[67] and dioctyltin bis (isooctylthioglycollate) has been shown to be an effective catalyst for the decomposition of hydroperoxides[67,77,78]. Like most sulphur compounds, it shows two stages of peroxide decomposition. During the first stage a stoichiometric oxidation of the sulphide occurs and this is followed by the catalytic destruction of hydroperoxides by the products in an ionic process.[46,50,67,79] The formation of antioxidant sulphur acids from the parent thioltin stabiliser plays the major role in the second stage catalytic ionic decompositiion of hydroperoxides.

The antioxidant effects of the products of peroxide decomposing agents, which is common to most sulphur stabilisers, makes the mechanism of stabilisation of these derivatives complex. This additional peroxidolytic antioxidant function of dioctyltin bis (isooctylthioglycollate) is responsible for its relatively high thermal antioxidant activity during oven ageing at 140°C compared with dibutyltin maleate under the same conditions.[67].

1.3.5 **Ultraviolet Stabilisation of PVC**

Ultraviolet light can be one of the most serious causes of polymer deterioration in service and unless measures are taken to prevent it, the effects may in some cases be catastrophic. Pure PVC contains no structures capable of absorbing sunlight and should be stable. In practice the polymer is quite susceptible to photo-degradation owing to the presence of various chromophoric groups. The susceptibility of PVC to photo-degradation is greatly increased by thermo-mechanical processing which rapidly introduces hydroperoxides and peroxy gel, unsaturation and carbonyl groups[30] into the polymer; all structures which are capable of initiating photo-chemical reactions leading to degradation. The important role of a good thermal stabiliser in promoting photo-stability by preventing formation of these photo-prodegradant structures has been adequately recognised.[30,66,79]

Dibutyltin maleate has been known to function as a photo-stabiliser in processed samples[80]. The function of the stabiliser is to eliminate the formation of polyconjugated unsaturation and of peroxides during thermal processing;[27] a function which persists to the photo-oxidation stage[77,80]. Although organotin compounds are outstandingly good thermal stabilisers the requirements in the stabiliser under photo-oxidation assume a different order of priority from those required for purely thermal stabilisation[81]. Thus, dibutyltin and dioctyltin bis (benzyl fumarates) are good thermal stabilisers but actually promote photo-degradation.[82] The dialkyltin bis (isooctylthioglycollates) are also slightly inclined to promote photo-degradation[66,67,77,79] whereas the maleate ester derivatives[66,67,77,79,83] or synergistic mixtures of polymeric organotin maleates with alkyltin mercapto-esters[84] are quite good photo-stabilisers. In all cases, however, much more effective photo-stability is achieved if a u.v absorber is also incorporated in the formulation.[66,79,85,86]

1.4 Polymer Oxidation and Conventional Antioxidants

The oxidation of PVC, like all oxidative degradation processes, follows the same scheme as the uninhibited oxidation of hydrocarbons originally proposed by Bolland[87] and Bateman[88]. The initiation process involves the production of free radicals (9) which may be formed by thermal energy, ultraviolet radiation, mechanical shear or by other initiators. Mechanical shear leading to polymer chain scission constitute a major source of radical generation during processing of polymers. The alkyl radical reacts rapidly with oxygen to produce

$$\text{Polymer} \longrightarrow R^{\bullet} \qquad (9)$$

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet} \qquad (10)$$

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet} \qquad (11)$$

alkylperoxyl radical (10), the latter species abstracting hydrogen from the polymer molecule to produce an alkyl hydroperoxide and a free radical which is capable of propagating the reactions (11). For most polymers, reaction (11) is rate determining and hence the radical present in highest concentration in the system is alkylperoxyl $RO\dot{O}$[89]. The consequence of this is that termination of the oxidation chain normally occurs predominantly by reaction of this species. For example, in the absence of an antioxidant, reaction (12) is the process primarily responsible for termination. At low oxygen pressures, however, or at high rates of initiation where oxygen diffusion into the systems is rate determining, reactins (13) and (14) become much more important[89].

$$2ROO^{\bullet} \longrightarrow \text{stable products} \qquad (12)$$

$$ROO^{\bullet} + R \longrightarrow ROOR \qquad (13)$$

$$2R^{\bullet} \longrightarrow R - R \qquad (14)$$

It follows therefore that alkyl radicals are important during processing under closed mixer where the only oxygen present is that initially trapped in the polymer. In the presence of excess oxygen as occurs during processing in an open mixer, thermal ageing in an air-driven oven, or under atmospheric weathering and photo-oxidative conditins in laboratory u.v. cabinets, the reaction of alkyperoxyl radical predominates.

1.4.1 Antioxidants

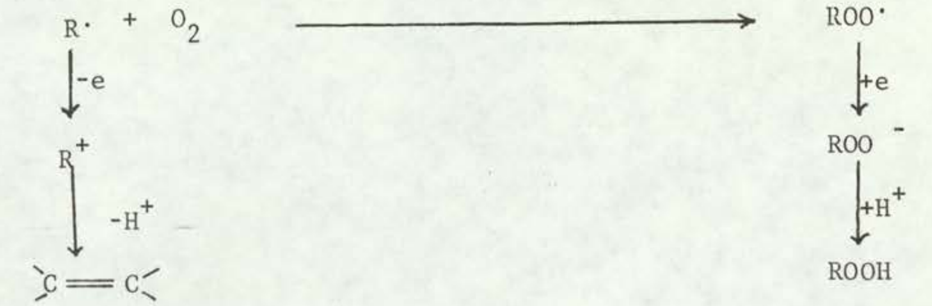
Antioxidants may be defined as agents which are added to polymers to inhibit oxidative deterioration either during processing or in service.

Scott[44] showed that two mechanistically distinct classes of antioxidants can be distinguished in principle on the basis of the autoxidation process (9-11). The first type, which embraces the aromatic amines and phenols, operates by a radical chain-breaking (CB) mechanism by removing from the autoxidising medium the two important species normally involved in the propagating steps, i.e. the alkyl ($\dot{R}$) and alkylperoxyl($ROO^{\bullet}$) radicals. The second type, the preventive mechanism, which includes hydroperoxide decomposers, transition metal deactivators, u.v. stabilisers (acting by the u.v. light absorption mechanism) and excited state quenchers, is concerned not with the propagation reaction but with preventing the introduction of chain initiating radicals into the system.

1.4.2. **Chain Breaking Antioxidants**

The free radical chain reaction (9-11) can be interrupted by removal of either alkyl or alkylperoxyl radicals. These alternative oxidative and reductive mechanisms are outlined in scheme 3.

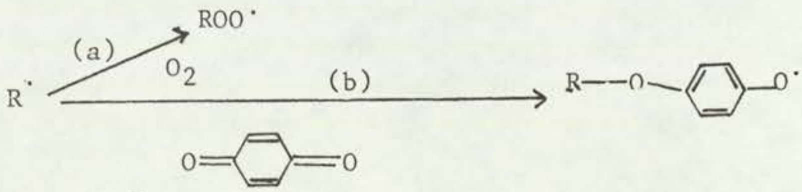
Scheme 3: Chain-breaking (CB) mechanism of antioxidants



Electron acceptor mechanism (CB-A)

Electron donor mechanism (CB -D)

Alkyl radical deactivators are electron acceptors (CB-A) which oxidise the radical to a carbonium ion, which may subsequently give an olefin by loss of a proton. In general, the molecular requirements for a CB-A antioxidant are the same as for polymerisation inhibitors,[44] the effectiveness of which probably depends on the efficiency with which the antioxidant can compete with oxygen for the alkyl radical (15). This class of antioxidants includes quinones, nitro compounds and

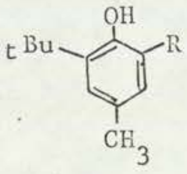


(15)

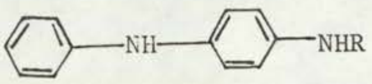
stable free radicals of which nitroxyls[90-95] and phenoxyls[96] have been widely studied.

Melt stabilisers acting by the CB-A mechanism are relevant to the stabilisation of PVC during thermal processing as these additives are capable of trapping macroalkyl radicals which are produced by the mechanochemically-induced rupture of polymer chains particularly under restricted oxygen availability. Although organotin stabilisers are widely used as thermal stabilisers for PVC, their actual participation in radical mechanism has not been reported as such. However, lubricants and other processing aids are incorporated into PVC formulations which improve the processing stability presumably by reducing the shearing forces acting on the polymer chain.

Alkylperoxyl radical deactivators are electron donors (CB-D) which reduce the alkylperoxyl radical to hydroperoxide via the corresponding anion (scheme 3). Hindered phenols (IV) and aromatic amines, notably the p-phenylene diamine (V) are the two best known classes of commercial antioxidants that exhibit the CB-D mechanism. Both classes are able to donate a hydrogen to an alkylperoxyl radical (16). The reaction with alkylperoxyl radicals involves the transition state (VI)



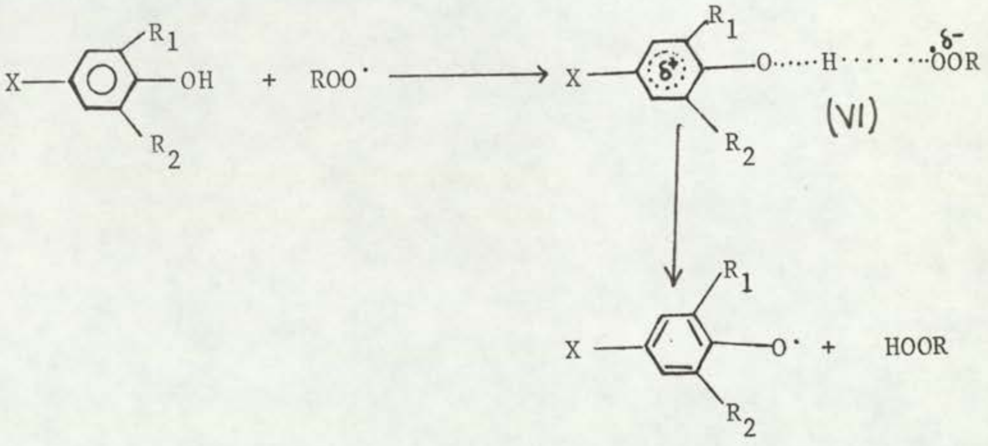
(IV)



(V)

and the effects of substituent groups in the aromatic rings is to alter the energy of the transition state which involves electron transfer to the peroxyl and electron delocalisation in the aromatic ring (17). Electron releasing and electron delocalising substituents reduce the energy of the transition state and thus increase the antioxidant activity.[44,75] The products formed by further reaction of the

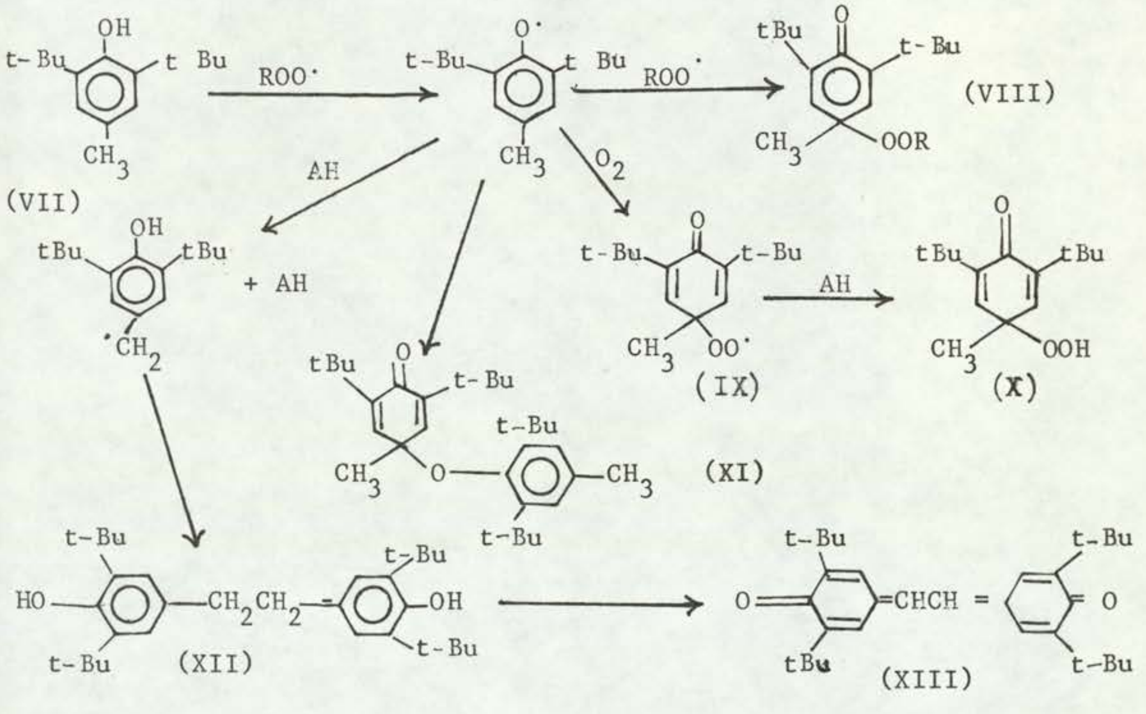
$$ROO^{\bullet} + AH \longrightarrow ROOH + A^{\bullet} \qquad (16)$$



(17)

initially formed phenoxyl radical are complex and may have either antioxidant or pro-oxidant acitivity (scheme 4)[75,97,98] The products of the reaction includes ethylene bisphenol (XII) which is as effective an antioxidant as the initial phenol (VII); stilbenequinone (XIII) is also effective although it functions by a complimentary (CB-A) mechanism and peroxydienones (VIII), (X) which are potential pro-oxidants due to the presence of the labile peroxide bond. Stilbenequinoid products (XIII) have also been found to be formed during processing and are considerably superior in antioxidant activity to the parent phenol (VII) under conditions where loss of antioxidant is important.[99] Secondary oxidation products formed from aromatic amines are also very powerful antioxidants[97] and in particular nitroxyl radicals have become of immense importance in the stabilisation of polymers.

<u>**Scheme 4:**</u> **<u>Transformation products of a hindered phenolic antioxidant</u>**[75]

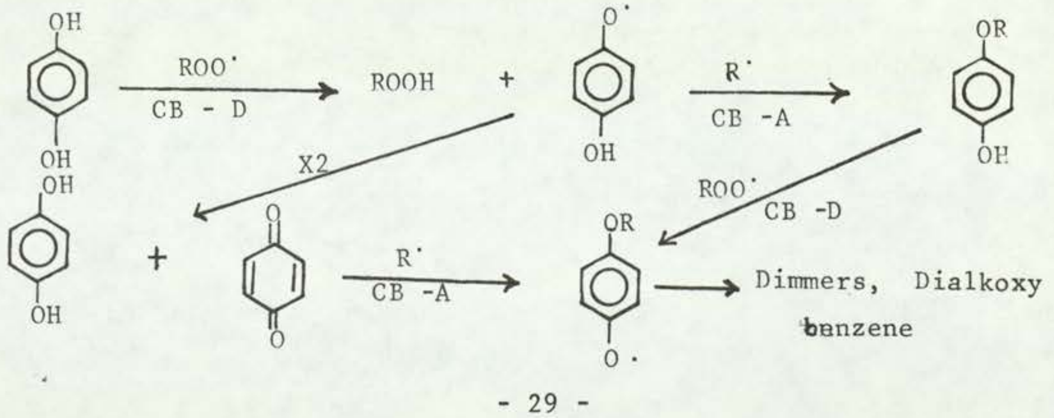


1.4.3 Complementary Antioxidants Involving both CB-A and CB-D

CB-A antioxidants operate best in an atmosphere of oxygen deficiency or at high initiation rates; that is, in an alkyl radical predominance whereas CB-D antioxidants function most efficiently when alkylperoxyl radicals are the major chain propagating species present in highest concentration in the antoxidising system. Antioxidants which exhibit both CB-A and CB-D are therefore clearly superior to those which operate by a single mechanism since in most oxidation and technological processes, both alkyl and alkylperoxyl radicals are present to some extent. A number of antioxidants are known which involve both CB-A and CB-D mechanisms.

Hydroquinone is known to be converted to benzoquinone by the CB-D mechanism (scheme 5)[75]. However, the resulting benzoquinone is itself a very effective alkyl radical trap and many radicals may be removed from the autoxidising system before antioxidant -inactive products are finally obtained. This mechanism accounts for the well known fact that hydroquinone is a much more effective inhibitor of polymerisation in the presence of a small amount of oxygen than in its complete absence whereas benzoquinone itself is equally effective in the complete absence of air.

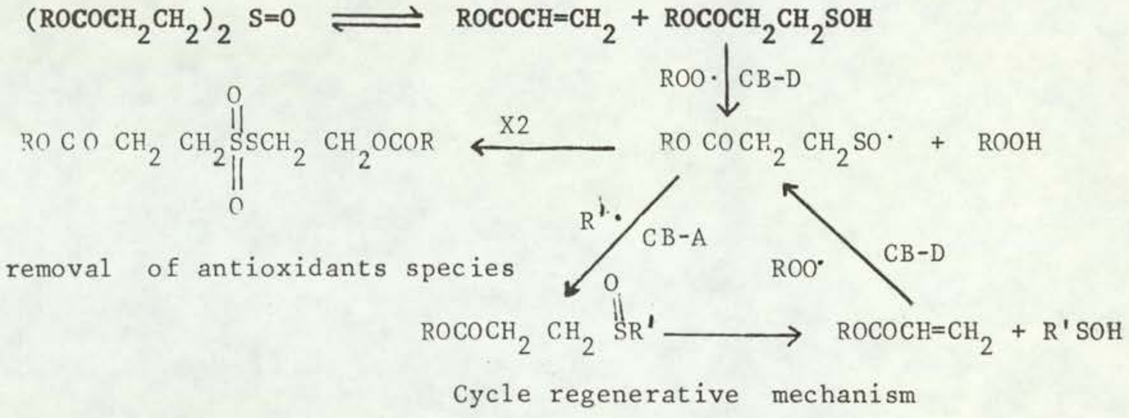
Scheme 5: **Complimentary mechanisms involving hydroquinone and its oxidation products[75].**



1.4.4 Regenerative Chain Breaking Antioxidants

In autoxidising systems where both R' and ROO' are present, some chain-breaking antioxidants have the ability to alternate between the oxidised and reduced states and hence exhibit regenerative behaviour. Sulphoxides such as dilaurylsulphinyl dipropionate are very effective melt stabilisers for polypropylene[52], and their known chemistry is consistent with the cyclical process, scheme 6.

Scheme 6: Sulphoxides as regenerative antioxidants[79]



The photostabilisation of paint films by copper ions has been shown[100] to involve a very similar cyclical process. Experimental evidence[90,91] also suggests that a similar cyclic regenerative process involving the nitroxyl radical is involved in the photostabilisation of polyolefins by hindered piperidines in which the parent amine is converted during processing into the corresponding nitroxyl radical. The detailed chemistry of the regeneration reaction is however not yet clear and further confirmatory evidence is required. Although regenerative antioxidants have been widely investigated in polyolefins, such studies in PVC are scarce.

1.4.5 Preventive Antioxidants

Hydroperoxides are the most important products of the cyclical autoxidation process since they are the main source of further radicals in the system. Hydroperoxides are both thermo and photo-unstable, giving rise to alkoxyl and hydroxyl radicals (see scheme 7). The latter species react rapidly with hydrocarbons to give macroalkyl radicals which feed back into the main autoxidation cycle thus maintaining the chain mechanism. Transition metal ions capable of undergoing one-electron redox reaction and a variety of reducing agents undergo redox reaction with hydroperoxides thereby increasing the rate of radical generation in the autoxidising system. Agents which decompose hydroperoxides by a process which does not give rise to free radicals (PD) or which in some way stabilise hydroperoxides e.g. by absorbing u.v. irradiation (UVA), or by deactivating transition metal ions (MD) prevent the re-initiation of the chain reaction and are classified generally as preventive antioxidants[75] (see scheme 7). The most important of the preventive antioxidants act by the peroxide decomposing mechanism[79,101] since hydroperoxides are universally involved in autoxidation irrespective of the enviroment[81].

Peroxide decomposers fall into two main mechanistic classes[75]: stoichiometric reducing agents (PD-S) and catalysts for peroxide decomposition (PD-C). The main requirement of compounds falling into the PD-S class is that they should substantially reduce hydroperoxides to alcohols without the substantial formation of free radicals. Phosphite esters[51,75] are the most widely used PD-S antioxidants in rubber. A wide variety of sulphur compounds fall into he PD-C class.

These compounds have in commonn the ability to destroy hydroperoxides through the formation of an acidic product (a sulphur oxide or acid) in a radical generating reaction involving the hydroperoxide. In all cases the antioxidant function is preceded by a pro-oxidant stage. Examples of PD-C antioxidants include metal dithiocarbamates, dithiophosphates [75,76,102] and thiols, mono and disulphides[44,48-50,75,76,102]

Thioltin compounds used as melt stabilisers for PVC during processing are known to function as catalysts for hydroperoxide decomposition.[65,77,79] The additional peroxidolytic antioxidant function of these stabilisers is also suggested as being responsible for their relatively higher thermal oxidative (oven ageing) antioxidant activity than dibutyltin maleate stabilisers under the same conditions[67]. Moreover, reaction products of thioltin stabilisers - sulphur acids - are also known to catalytically decompose hydroperoxides[79].

1.5 Mixed Stabilisers and Synergism

The requirements for antidegradants under different conditions differ and are often conflicting and as such there is practical interest in the development of multi-component stabilising systems for polymers. Various sources of initiating the degradation of polymers and the possible ways and stages of intervention by the incorporated antidegradants are outlined in scheme (7). It is important to emphasise that effective stabilisation often requires that a combination of antioxidant sytems be involved; so also is the fact that a single antioxidant may act by a number of the mechanisms shown in scheme (7). Indeed, more often than not, the overall stabilising effectiveness of an antioxidant derives from a complementary overlap of different mechanisms by which it acts together with its oxidation products and intermediates.

The phenomenon of synergism may be defined as a cooperative action between antioxidants such that their total stabilising effect is greater than the sum of the individual effects alone. Scott[44] credited Mattil and co-workers[103,104] with the original recognition of this "greater than additive effect" of a combination of antioxidants in their studies on the difference in response of vegetable and animal fats to added antioxidants. The differences observed were attributed to the presence of adventitious naturally occuring antioxidants which in some cases powerfully augmented the action of other protective agents.

Two mechanistically distinct types of synergism have been outlined[44]. Homosynergism, involving two compounds of unequal activities but operating by the same mechanism; and hetero-synergism, arising from the cooperative effects of antioxidants acting by different mechanisms. The combined action of two chemically similar compounds to give an antioxidant effect greater than might have been expected on the basis of their individual activities is a well known and in many cases technologically important phenomenon[105]. For phenolic antioxidants of this type for example, the weaker antioxidant serves as a reservoir for re-furnishing the more active antioxidant which traps the radical species in the autoxidising media by hydrogen transfer to the active antioxidant product. In the latter category are combinations of chain breaking (CB) with preventive antioxidants of various types. Both qualitative and quantitative aspects of the synergism of such combinations have been reviewed by Reich and Stivala[59]. A practically important aspect of synergism occurs when two or more types of antioxidant function are associated in the same antioxidant molecule - a phenomenon referred to as autosynergism.

The very different antioxidant requirements for oxygen excess and oxygen deficiency make the design of single component chain-breaking antioxidants for processing and service life very difficult even by the use of regenerative antioxidants. The light stable peroxide decomposers on the other hand appear to satisfy many of the requirements of the ideal multi-purpose single-component antioxidant; they are effective melt stabilisers and because of their non-volatility they impart excellent thermal oxidative ageing stability. They are also among the more effective single component light stabilisers known.[81] Their only major disadvantage is the rather intense colour they impart to the polymer and this defect constitutes a significant deterence for the use of some of these PD antioxidants in PVC where colour stability is a priority.

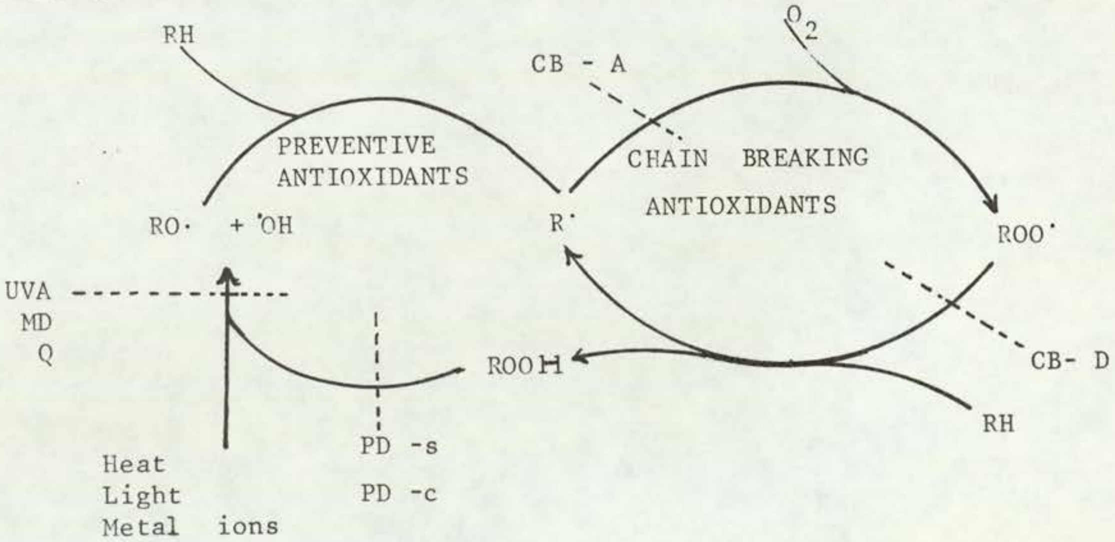
The broad spectrum of activity of PD antioxidants confirms the key importance of hydroperoxides in all types of oxidative degradation processes and makes the search for a non-coloured analogue of the transition metal thiolates a very viable alternative to the multi-component stabilising system for the thermoplastic hydrocarbon polymers currently in commercial use.

1.5.1 Antioxidants and Mechanisms of Antioxidant Action

Scheme (7) outlines the free radical chain reaction originally developed for low molecular weight olefins by Bolland[87] and Bateman[88] but subsequently applied successfully to a range of polymers.[44,59,106,107] The scheme represents a summary of antioxidants and their mechanisms of action, some of which have been discussed above. It may be seen that the stabilisation of polymers is a complex technology with different molecular requirements under different technological conditions, requirements which are in some cases conflicting. The cyclical radical process can be interrupted by the removal of either alkyl or alkylperoxyl radicals through oxidative and reductive mechanisms respectively.

Chain breaking and preventive antioxidants interfere at different points in the autoxidation process (see scheme 7) and as such they mutually reinforce one another. This not only leads to a greater antioxidant effect than the sum of the effects of each antioxidant alone (synergism). But, as well as being complementary in mechanism, the two classes of antioxidants frequently complement each other in their combined response to enviromental conditions and the use of these two mechanistic types of antioxidants together gives rise to protection over a broader spectrum of technological and enviromental conditions than either type alone. It may be predicted therefore that the future of the stabilisation technology of polymers, and in particular of PVC,

Scheme 7: General Antioxidant Mechanisms[108,109]



CB-A -	Chain breaking (acceptor); CB-D-chain breaking (donor);
PD-S -	Peroxide decomposer (stoichiometric); PD-C-Peroxide decomposer (catalytic);
UVA -	Ultra violet absorber; MD - Metal deactivator;
Q -	Quencher (of excited states).

depends to a large extent on the development of more effective synergistic antioxidant systems. In terms of optimisation and cost-effectiveness which is of primary concern to industrialists, it is anticipated that synthesis of autosynergists will most probably attract more research and development in the years ahead.

1.6 Purpose of this Research

Previous studies[27-30] have shown that unstabilised PVC undergoes substantial loss of HCl during processing with concomitant formation of olefinic unsaturation and hydroperoxides. The initial mechano-chemical process sensitizes the polymer to subsequent thermal degradation.[28] Peroxides in association with unsaturation formed during processing are also known to initiate the polymer to photo-oxidation[30]. There is therefore considerable practical interest in devising heat and light stabilisers for PVC.

The effects of lubricants (Wax E, a commercial ester lubricant and Calcium stearate) and Dibutyltin maleate (DBTM) stabiliser on the mechano-chemical and thermal degradation of PVC during processing have been studied[27]. The protective mechanism of the two types of additive were found to be complementary in that the lubricants reduced the severity of the mechano-chemical shear inflicted on the polymer chains whereas the tin maleate stabiliser reduced the rate of hydrogen chloride elimination during the second stage by reacting with both allylic chlorine and hydrogen chloride as well as with conjugated unsaturation.

One objective of this research is to investigate the effect of lead stearate and of partial replacement of DBTM with commercial phenolic antioxidants Irganox 1300, 1076 and 1010 on the processing and thermal oxidative stability of PVC. This study will be done in the presence of Wax E/CaSt lubricant mixture and DBTM as the standard thermal stabiliser to which other results may be compared.

Hindered piperidines have been widely reported as photostabilisers for polyolefins[90-95] but similar studies in PVC are scarce. The photostabilising activities of 2,2,6,6-Tetramethyl piperidine, its derived nitroxyl radical and hydroxylamine, Bis (2,2,6,6-tetramethyl piperidinyl) sebacate and its derived bisnitroxyl, will be investigated in PVC and their effects compared with that of a commercial u.v. absorber, 2-Hydroxyl-4-octyloxyl benzophenone. The exceptional efficiency of hindered piperidines as melt stabilisers in polypropylene has been explained in terms of cyclic regenerative mechanism which results from the participation of the complementary chain-breaking donor (CB-D) and chain-breaking acceptor (CB-A) antioxidant mechanisms involving both the nitroxyl radical and hydroxylamine derived from the parent amine.[189,109] Evidence for the mechanism of stabilisation of these compounds in PVC will also be investigated.

The role of α, N-Diphenyl and α-Phenyl-N-methyl nitrones, 2-Methyl-2-nitroso propane, 1,3-Dihydroxyl-2-hydroxylmethyl-2-amino propane, 1,3-Dihydroxyl-2-hydroxylmethyl-2-nitrone propane and its stearyl, lauryl, oleayl and propionyl esters will also be examined as photostabilisers in PVC. The esters of the nitro compound are proposed for investigation because it is anticipated that by increasing the alkyl chain and hence the molecular weight of the compouond, its solubility in PVC during processing may not only be increased but its loss during subsequent ageing may also be reduced.

CHAPTER TWO

EXPERIMENTAL

2.1 Materials

Materials and experimental methods used during the course of this research are described in this chapter. General purpose reagents and solvents were supplied by the Chemistry Department Stores and used without further purification. Detailed description of these materials has been omitted in the following sections.

2.1.1 Polymer

Breon PVC M90/50 homopolymer was supplied by British Petroleum Limited. This grade was obtained in the unstabilised powder form, free of additives. Gel permeation chromatography of the polymer gave the following molecular weight details:

$$\overline{M}n = 30740; \ \overline{M}w = 74120; \ \overline{M}z = 187900; \ \overline{M}v = 67500$$

$$\overline{M}w/\overline{M}n = 2.41 \ ; \ \overline{M}z/\overline{M}n = 6.11$$

The density of the polymer was found to be $1.4 g/cm^3$.

2.2 Commercial Stabilisers

Dibutyltin maleate-based stabiliser, Irgastab T290 was supplied by Ciba-Geigy Limited and was a white dusty solid of M.P. 106°C and M.W. 346.82.

Elemental analysis of this material gave:

	Sn	C	H
Calculated for $SnC_{12}H_{20}O_4$:	Sn, 34.22;	C, 41.55;	H, 5.77
Found	34.18;	41.62;	5.72

Infrared spectroscopy of a toluene solution gave:

2915 cm^{-1} (aliphatic C-H stretching); 1725 cm^{-1} (unsaturated ester); 1605 cm^{-1} (ester conjugated C = C).

<u>UV 531</u> 2-Hydroxyl-4-octyloxyl-benzophenone was supplied as Cyasorb UV531 by Cyanamid Corporation and was a light yellow cystalline solid, M.P. 47°C and M.W. 326.21.

Elemental analysis of this material gave:

	C	H
Calculated for $C_{21}H_{26}O_3$	C, 77.32;	H, 9.97
Found	74.44;	9.90

Infrared spectroscopy of a hexane solution gave:

3450 cm^{-1} (hydroxyl bonded OH stretch); 2915 cm^{-1} (aliphatic CH stretch)

1740 cm^{-1} (hydrogen bonded ketone); 1620 cm^{-1} (aromatic absorption).

Tinuvin 770 Bis (2,2,6 6-tetramethyl-4-piperidinyl) sebacate, commercially known as Tinuvin 770 was supplied by Ciba-Geigy, M.P.82-85 °C; M.W. 480

Elemental analysis of this material gave:

Calculated for $C_{28}H_{52}N_2O_4$: C, 70.0; N, 5.83; H, 10.83
Found 68.8; 5.6 ; 11.2

Tris Nitro and Amine 1,3-Dihydroxyl-2-hydroxymethyl-2-nitropropane and 1,3-Dihydroxyl-2-hydroxymethyl-2-amino propane are commercial samples supplied as Tris Nitro and Tris Amine respectively by Angus Chemie. Elemental analysis gave:

Calculated for (Tris Nitro) $C_4H_9NO_5$: C, 31.79; N, 9.27; H, 5.96
Found 32.2 ; 8.6 ; 6.1
Calculated for (Tris Amine) $C_4H_{11}NO_3$: C, 39.67; N,11.57 ; H, 9.09
Found 40,3 ; 10.7 ; 8.8

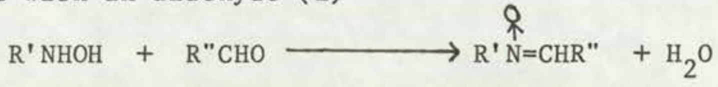
Lead Stearate Lead Stearate was supplied by Fisons Limited, M.W. 774 and M.P. 115.7°. Elemental analysis gave:

Calculated for Pb $(C_{18}H_{35}O_2)_2$, Pb, 26.74; C, 55.81; H, 9.06
Found 25.8 ; 56.1 ; 9.5

Lubricants Calcium stearate supplied by Fisons Limited and Wax E, supplied by Hoechst AG, were used as lubricants in PVC formulations. Phenolic antioxidants, (3,5-di-t-butyl-4-hydroxylphenyl)propionate (Irganox 1300), octadecyl 3-(3,5-di-t-butyl-4-hydroxyl phenyl)propionate (Irganox 1076), and tetrakis methylene 3-(3,5-di-t-buthyl-4-hydroxylphenyl)propionate (Irganox 1010) was supplied by Ciba-Geigy and used without further purification.

2.3 Synthesis of Stabilisers

Aliphatic and aromatic nitrones were prepared by the reaction of an hydroxylamine with an aldehyde (1)



$$R'NHOH + R''CHO \longrightarrow R'\overset{\overset{O}{\uparrow}}{N}{=}CHR'' + H_2O \qquad (1)$$

2.3.1 α - Phenyl-N-methylnitrone

a) N-Methylhydroxylamine hydrochloride was prepared by the method of Beckmann.[110] Nitromethane (100g), ammonium chloride (60g) and water (800 ml) were stirred for 3 hr. at 11-14° with gradual addition of 275g zinc dust. An exotherm caused by rapid addition of zinc was avoided by controlled and slow addition over a period of 2 hr. The reaction mixture was filtered and neutralised with conc. HCl. Evaporation of the solution gave a yellow hygroscopic solid which was dried over KOH. Repeated recrystallisations from boiling absolute ethanol and ethylacetate followed by washing with dry ether gave white cyrstals, M.P. 88°C (88-89).[110]

b) Benzaldehyde (26g) was suspended in 2N NaoH (140 ml) by mechanical stirring and N-methylhydroxylamine hydrochloride (22g in 50ml water) was added. The mixture was stirred for 30 min and the nitrone remaining in solution was extracted thrice with cloroform (40 ml aliquots). The solvent was removed on a water bath and then by vacuum drying. The product solidified on cooling and was storred over KOH for 4 days. Recrystallisation from benzene and 60/80 petroleum ether gave white crystals, 8.26g (25% yield), M.P. 82°C (82).[111]

Infrared analysis (KBr disc) gave:

1594 cm^{-1}, S(C=N stretch); 1419 cm^{-1}, S(CH in-plane bend);
1180 cm^{-1}, M.S(Ph-C stretch; 1168 cm^{-1}, S(N-O stretch)
944 cm^{-1}, M.S(C-N stretch)

Elemental analysis of this product gave:

Calculated for C_8H_9NO	C, 71.1	H, 6.7	N, 10.3
Found	71.3	6.5	10.2

2.3.2. α, N-Diphenylnitrone

a) N-Phenylhydroxylamine Nitromethane (41.6 ml), ammonium chloride (25g) and water (800 ml) were stirred vigorously in a beaker for 15 min. Zinc dust (59g) was added with stirring over a period of 15 min. The rate of addition of zinc was such that the temperature rose rapidly to 62-63°C and remained stationary until all the zinc had been added. Stirring was continued for a further 15 min by which time reaction was complete, evidenced by a fall in temperature. The warm reaction mixture was filtered to remove ZnO and then washed with 100 ml of hot water. NaCl (150g) was added and the filtrate was cooled in an ice/salt mixture for 1 hr. Pale yellow cyrstalls which formed were filtered and recrystallised from benzene and 40/60 petroleum ether to give the pure compound M.P. 81°C (81.)[112] Due to its instability to oxidation, this product was used freshly prepared or kept refrigerated before use, but not longer than 48 hr.

b) N-Phenylhydroxylamine (10.9g) and benzaldehyde (10.6g) were dissolved in minimum methanol and allowed to stand overnight. The precipate which formed was filtered, washed with a little methanol and dried. Recrystallisation from methanol gave white crystalls M.P. 113°C (112-113)[113], (114-115).[114]

Infrared analysis (KBr disc) gave:

1548 cm^{-1}, S (C=N stretch) ; 1398 cm^{-1}, S (CH in-plane bend);

1191 cm^{-1}, S (Ph-N stretch); 1067 cm^{-1}, S (N-O strech);

887 cm^{-1} M.S. (CH out-of-plane bend)

Elemental analysis of this product gave:

Calculated for $C_{13}H_{11}NO$:	C, 79.1;	H, 5.6;	N, 7.1
Found	79.3	5.5	7.0

2.3.3. α-4-Hydroxylphenyl-N-phenylnitrone

N-Phenylhydroxylamine (10.9g) and 4-hydroxylbenzaldehyde (12.2g) were dissolved in minimum methanol and allowed to stand overnight. A pale yellow precipitate formed and was filtered, washed with methanol and dried under vacuum at room temperature. Recrystallisation from methanol gave the nitrone,

M.P. 211°C (212).[115]

Infrared analysis (KBr disc) gave:

1605, 1575cm^{-1}, S (Ph ring); 1191cm^{-1}, S (Ph-N stretch);

1080cm^{-1}, shoulder (coupled N-O stretch); 1060cm^{-1} S (N-O stretch);

887cm^{-1}, M.S (CH out-of-plane bend).

Elemental analysis of this product gave:

	C	H	N
Calculated for $C_{13}H_{11}NO_2$:	C, 73.2;	H, 5.2;	N, 6.6
Found	72.8	5.4	6.5

2.3.4 α- (3,5-Dimethyl-4-hydroxylphenyl)-N-phenylnitrone

a) Dimethyl-4-hydroxylbenzaldehyde was prepared by the method of Nikiforov and co-workers.[116]

Hexamethylene tetramine (25g), boric acid (35g) and ethylene glycol (100ml) were heated to 130°C in a beaker with stirring. 2,6-xylenol (12.2g) was added over a period of 15 min. after which stirring and heating was continued for a further 30 min. A colour change to deep orange was observed after which the beaker was removed from heat and cooled slightly (80°-90°). Sulphuric acid (150 ml, 30% v/v) was then added and the mixture allowed to stand for 1hr. The aldehyde precipitated and was filtered. Recrystallisation from aqueous methanol gave needles, M.P. 114°C (113).[114]

b) N-Phenylhydroxylamine (10.5g) and 3,5-dimethyl-4-hydroxylbenzaldehyde (15g) were dissolved in minimum methanol and allowed to stand overnight. A cream precipitate formed. Recrystallisation from methanol gave yellow crystals. M.P. 168°C.

Infrared analysis (KBr disc) gave:
3100 - 3400 cm^{-1}, B (OH group) ; 1570 cm^{-1}, S (C=N stretch);
1390 cm^{-1}, M.S. (C-H bend, CH_3); 1191 cm^{-1}, S (Ph-N stretch);
1150 cm^{-1}, V.S. (C-O stretch); 1075, 1060 cm^{-1}, V.S (N-O stretch);

Elemental analysis of this product gave:

Calculated for $C_{15}H_{15}NO_2$: C, 74.6 H, 6.2; N, 5.8

· 74.9 6.1 5.7

2.3.5 α - (3,5-Dimethyl-4-hydroxylphenyl)- N-methylnitrone

N-Methylhydroxylamine hydrochloride (11g in 20 ml water) was added to 3,5-dimethyl-4-hydroxylbenzaldehyde (16g) suspended in 2N NaOH. Orange colouration developed as the mixture was stirred. Stirring was continued for 2 hr. after which conc. HCl was added to neutralise the solution (pH 6.5). On standing, a yellow precipitate formed and was recrystallised from methanol to give white crystals. M.P. 205°C (206)[114]

Infrared analysis (KBr disc) gave:

3100-3300 cm^{-1}, B (OH group); 1580 cm^{-1}, S (C=N stretch); 1410cm^{-1},S(CH in-plane bend); 1390cm^{-1}, M.S(CH_3 sym deformation); 1168, 1140 cm^{-1}, S (N-O stretch)

Elemental analysis of this product gave:

Calculated for $C_{10}H_{13}NO_2$: C, 67.0, H, 7.3, N, 7.8

Found 66.7 7.4 7.8

2.3.6 α-(3-t-Butyl-5-methyl--4-hydroxylphenyl)-N-phenylnitrone

a) 3-t-Butyl-5-methyl-4-hydroxyl benzaldehyde was prepared in a similar way to 3,5-dimethyl-4-hydroxylbenzaldehyde by using 2-t-butyl-6-methylphenol instead of 2,6-xylenol. After recrystalisation from aqueous methanol, pale pink crystalls were obtained, M.P. 153°C.

b) N-Phenylhydroxylamine (11g) and 3-t-butyl-5-methyl-4-hydroxylbenzaldehyde were dissolved in minimum methanol and allowed to stand overnight. A yellow precipitate formed which ws recrystallised from aqueous methanol, giving yellow crystals, M.P. 195°C
Infrared analysis (KBr disc) gave:
3100-3500 cm^{-1}, B (OH group); 1595, 1560 cm^{-1}, S (Ph-ring);
1550 cm^{-1}, M.S. (C=N stretch); 1398 cm^{-1}, M.S (CH in-plane bend);
1360 cm^{-1}, W (CH_3 sym. deform); 1067 cm^{-1}, V.S. (N-O stretch);
870 cm^{-1}, M.S (CH out-of-plane bend).

Elemental analysis of this product gave:

Calculated for $C_{18}H_{21}NO_2$:	C, 76.3;	H, 7.4;	N, 5.0
Found	77.0	7.2	4.9

2.3.7 α-(3-t-Butyl-5-methyl-4-hydroxylphenyl)-N-methylnitrone

N-Methylhydroxylamine hydrocloride (5.5g in 15ml water) was added to 3-t-butyl-5-methyl-4-hydroxylbenzaldehyde (12.5g) suspended in 2N NaOH. The mixture was stirred for 3 hr after which the solution was neutralised with conc. HCl. A yellow precipitate which formed was filtered and recrystallised from methanol, giving yellow crystals, M.P. 144-145°C

Infrared analysis (KBr disc) gave:
3210 cm^{-1}, V.B (OH group); 1595 cm^{-1}, M.S.(C=N stretch);
1575 cm^{-1}, S (Ph ring); 1165,1180cm^{-1}, M.S.(t-butyl);
1172 cm^{-1}, S (N-O stretch); 944 cm^{-1}, M.S.(C-N stretch).

Elemental analysis of this product gave:

Calculated for $C_{13}H_{19}NO_2$:	C, 70.6,	H, 8.6,	N, 6.3
Found	70.5	8.5	6.3

Notations used for infrared spectra intensities:

S (strong); M.S. (medium strong); V.S. (very strong);
W (weak); B (broad) and V.B. (very broad)

All figures quoted for elemental analysis are per centages.

2.3.8 α - 3,5-Dimethyl-4-hydroxylphenyl-N-isopropyl nitrone

72.6ml of 2-Nitropropane and 30g ammonium chloride were dissolved in 400 ml of water and cooled in an ice-salt bath to below 20°C. 137.5g Zinc dust was added gradually with stirring over a period of 2-3 hr. Addition of zinc was regulated to avoid the temperature of the reaction mixture rising above 20°C. After complete addition of zinc, the mixture was further stirred for 45 min. at room temperature. The mixture was filtered and the filterate containing N-isopropyl hydroxylamine hydrochloride was used to prepare the nitrone without isolating this intermediate.

To the filterate containing N-isopropyl hydroxylamine hydrochloride, 20g of 3,5-dimethyl-4-hydroxylbenzaldehyde dissolved in 100ml of 2N NaOH was added and stirred for 1 hr. The reaction mixture was made up to pH8 by dropwise addition of con. HCl. The mixture was then stirred overnight; by which time a pale yellow precipitate had formed. Recrystallisation from methanol gave the nitrone, M.P. 195-196°C.

Elemental analysis of this product gave:

Calculated for $C_{12}H_{17}NO_2$:	C, 69.6;	H, 8.2;	N, 6.8
Found	68.8	8.3	7.0

2.3.9 2-Methyl-2-nitrosopropane

A solution of t-butylamine (52.3ml) and 4g $Na_2WO_4.2H_2O$ in 50 ml of water was cooled in an ice/salt bath. Hydrogen peroxide (166.7ml, 21% w/v) was added dropwise over a period of 1-2 hr. with stirring. Temperature was kept below 20°C by controlled addition of H_2O_2. After adding all the H_2O_2, stirring was continued for a further 30 min by which time a blue organic layer had formed. About 4g NaCl was added to break the emulsion and the organic layer was separated, washed with dil.HCl and dried over $MgSO_4$. Distillation gave the dark blue nitroso compound, B.P. 50-55°C. The distillate was kept in an ice bath until it solidified to give colourless crystals, M.P. 69-70°C.

Elemental analysis of this product gave:

Calculated for C_4H_9NO:	C, 55.2;	H, 10.3;	N, 16.1
Found	55.4	10.2	16.1

2.3.10 2,2,6,6- Tetramethyl-1-oxyl-4-piperidinol (TMPDO)

This compound was prepared by the oxidation of 2,2,6,6-tetrametyl-4-piperidinol, TMPD. 14g of TMPD was dissolved in 140 ml of water and 1.4g $Na_2WO_4.2H_2O$ was added. 35ml of H_2O_2 (3o% W/V) was added dropwise over a period of 10 min. with stirring. The reaction mixture was further stirred magnetically overnight by which time a reddish orange colouration developed. The solution was saturated with NaCl and then extracted repeatedly with diethylether. The ether phase was dried over $MgSO_4$ for 1hr. $MgSO_4$ and ether were removed by filtering and rotary evaporation respectively, leaving orange crystals of the product. Recrystallisation from diethyl ether gave crystals, M.P. 70°C (72).[77]

Elemental analysis of this product gave:

Calculated for $C_9H_{18}NO_2$:	C, 62.8;	H, 10.5,	N, 8.1
	62.9	10.7	9.1

Infrared analysis (KBr disc) gave:

3230 cm^{-1} (disappeareance of N-H stretch of parent amine);

1355 cm^{-1} (N-O stretch, new absorbance not shown in parent amine)

2.3.11 2,2,6,6- Tetramethyl-1,4-piperidinediol (TMPDOH)

This compound was prepared by the reduction of 2,2,6,6-tetramethyl-1-oxyl-4-piperidinol, TMPDO, by the method of Rozantsev and Golubev.[118]

85% hydrazine was added to a solution of 1.73g TMPDO in 10ml methanol. The reaction mixture was refluxed overnight at 70°C to achieve complete decolourisation. Methanol was removed under vacuum at room temperature. Recrystallisation of the residue from a mixture of ether and benzene (1:1) gave colurless needles, M.P. 157°C (157).[118]

Elemental analysis of this product gave:

Calculated for $C_9H_{19}NO_2$: C, 62.4; H, 10.9, N, 8.1

Found 62.3 10.7 8.0

Infrared analysis (KBr disc) gave:

1355 cm^{-1} (disappearance of band, N-O stretch);

1490 cm^{-1} (new absorption band, probalby due to N-OH stretch)

2.3.12 Bis (2,2,6,6-Tetramethyl-1-oxyl-4-piperidinyl) sebacate (ONNO)

To a solution of Bis (2,2,6,6-tetramethyl 1-4-piperidinyl sebacate, commercially known as Tinuvin 770, in 200 ml of ether, 8.1g m-chloroperbenzoic acid powder was added with stirring over a period of 1 hr. at room temperature. The reaction mixture was further stirred magnetically overnight by which time the colour of the solution was deep red. The solution was washed 4 times with 50 ml aliquots of 5% $NaHCO_3$ and the ether evaporated under reduced pressure and the orange red powder was recrystallised from absolute ethanol to give the product, M.P. 100-101°C (101).[119]

Elemental analysis of this product gave:

Calculated for $C_{28}H_{50}N_2O_6$: C, 65.8; H, 9.8, N, 5.5

Found 65.2 9.9 5.8

Infrared analysis (KBr) gave:

3600 cm^{-1} (dissapearance of band, N-H stretch);

1365 cm^{-1} (absorption of new band, $N-O^{\bullet}$ stretch)

2.3.13 Propionyl Ester of Tris Nitro (PETN)

15.1g (0.1 mole) Tris nitro was refluxed for 5 hr. with 23 ml (0.3 mole) of propionic acid in the presence of 2g toluene-p-sulphonic acid catalyst and 200 ml toluene as solvent in a Dean and Stark apparatus. The reaction was complete after 5.4 ml (0.3 mole) of water have been collected. Toluene was removed by rotary evaporation to obtain the product which was distilled to give a liquid, D (25°C) = 1.167 (1.171).[120]

Elemental analysis of this product gave:

Calculated for $C_{13}H_{21}NO_8$:	C, 48.9;	H, 6.6,	N, 4.4
Found	47.7	6.7	4.2

2.3.14 Lauryl Ester of Tris Nitro (LETN)

The procedure employed above for preparing the propionyl ester (section 2.3.13) was employed. 60.1g of lauric acid was used to give a product M.P. 33°C.

Elemental analysis of this product gave:

Calculated for $C_{40}H_{75}NO_8$:	C, 68.9;	H, 10.8,	N, 2.0
Found	C, 69.2	10.3	2.1

2.3.15 Oleayl Ester of Tris Nitro (OETN)

The procedure of section 2.3.13 was employed. 84.74g of oleic acid was used and a deep brown viscous liquid was obtained D(25°C) = 0.935

Elemental analysis of this product gave:

Calculated for $C_{58}H_{105}NO_8$: C, 73.8; H, 11.1, N, 1.5
74.2 10.8 1.4

2.3.16 Stearyl Ester of Tris Nitro (SETN)

The procedure of section 2.3.13 was employed 85.4g of stearic acid was used. The product obtained was washed several times with cold water and then dried to give M.P. 59°C.

Elemental analysis of this product gave:

Calculated for $C_{58}H_{111}NO_8$: C, 73.3; H, 11.7, N, 1.5
Found C, 72.8 12.1 1.4

2.4 Polymer Processing and Film Preparation

2.4.1 Polymer Processing

Prior to actual thermal processing, PVC formulations were tumble-mixed for the purpose of homogenisation . Processing of formulations was carried out in a RAPRA torque rheometer, MK11, which is a prototype internal mixer and consists of a mixing chamber built around two chromium-plated steel counter rotors driven electrically. The chamber was oil heated and thermostated, the required temperature being pre-set on a dial. A fitting air pressured ram, operated through the hopper permits the opening and closing of the mixing chamber at the hopper end. The chamber may be operated either open to the atmosphere or seated by means of the ram which provides a virtually air-tight seal.

The chamber may be opened for the removal of processed samples and for cleaning purposes.

A processing temperature of 180°C and rotor speed of 60 rpm were used for most of this work and the variation of torque generated with time during processing was monitored on the rheometer recorder. The processed polymer was rapidly withdrawn, chilled in water, dried and stored in sealed bags. The chamber, rotors ram and hopper were all carefully freed of contamination prior to each sample processing by cleansing with polystyreme.

2.4.2 Preparation of Polymer Films

The processed polymer was powdered and compression moulded between stainless steel glazing plates at 170°C for 3 min. using 550 PU grade cellophane to separate the polymer from the steel plates. The polymer was preheated between the plate~~r~~ns of an electrically heated press for 45 seconds prior to the application of a ram pressure of 25 kgm cm^{-2}. At the end of the pressing operation, the films were cooled rapidly by means of circulating water to the press platerns. Uniform films of thickness 5X10^{-3}cm were selected for thermal and uv analyses.

2.4.3 Oven Ageing of Polymer Films

Polymer films were subjected to thermal ageing in an air circulating (5ft^{3}h^{-1}) Wallace oven thermostatted at 140°C. The oven consists of six sample cylinders with the fitting lids containing suitable provision for sample support. Sample films were mounted on specially prepared cardboards and held in position by copper wire supports. A single sample was always placed in each cylinder (i.e. samples were aged separately) so as to prevent cross-contamination due to degradation products and antioxidants between films, which constitutes a serious limitation of conventional oven ageing tests in which samples are aged together. Individual ageing of films is also important in order to ensure reproducibility.

Chemical changes such as peroxide, unsaturation, colour, gel and carbonyl formation were monitored at intervals, batch uniformity being ensured by examining suitable control samples.

2.4.4 Ultra Violet Ageing of Polymer Films

Ultra violet irradiation of polymer films was performed in a sunlamp/blacklamp (S/B) cabinet consisting of a cylindrical casing containing an inner cylindrical rotating frame upon which the polymer specimens were mounted. Thirty-two fluorescent lamps were mounted on the inside of the cylindrical casing so that the samples rotated continuously past these lamps at a distance of 10 cm. The radiation source consisted of 24 Type C Phillips actinic blue Lamps (05) and 8 Type A2 Westinghouse sunlamps (FS20) symmetrically distributed so that 3 blue lamps alternated with 1 sunlamp. The fluorescent blue lamps gave a symmetrical spectra distribution from 300-400nm, peaking at 374 nm while the fluorescent sunlamps gave a symmetrical distribution from 280-400nm, peaking at 317 nm[121]. This combination has been found to correlate well with outdoor exposure tests.[30] The temperature inside the cabinet was standardised at 38 ± 2°C by means of a driven ventilator situated under the rotating frame. The cabinet is open to the atmosphere on both the lower and upper sides; the two sides being covered with perforated steel gauze.

To minimize the problem of decline in the intensity of the lamps output with time, a set of 4 tubes (3 actinic lamps and 1 sunlamp) was replaced sequentially after every 2000 hr. of exposure. At intervals, chemical changes occurring in the polymer films were monitored.

2.4.5 Molecular Weight Changes

Changes in molecular weight and molecular weight distribution in PVC samples were determined by gel permeation chromatography (GPC). Tetrahydrofuran, stabilised with 2,6-di-t-butyl-p-cresol, was used as solvent. Analysis was performed at 35^{o}C at a flow rate of 1ml/min and Mark-Houwink constants $K=1.5\times10^{-4}$, $\alpha = 0.77$ were used for conversion via Universal Calibration. All GPC analyses were done by RAPRA, Polymer Supply and Characterisation Centre, Shawbury.

2.5 Measurement of Functional Groups

2.5.1 Total unsaturation

The technique of Gallo, Wiese and Nelson[122] involving the mercuric acetate catalysed addition of iodine to double bonds was employed. 0.5g of powdered polymer was swollen in 75 ml of chloroform for 12 hr. in a conical flask fitted with a rubber seal. 5ml followed by 25ml of

0.1N iodine solution in chloroform and 25ml of mercuric acetate in glacial acid. The mixture was gently agitated for 1 hr. in the dark and 75 ml of 7.5% KI solution added. Excess iodine was titrated with 0.1N $Na_2S_2O_3$ and the starch end point noted in the aqueous phase. This method is not absolute since the rapid addition of iodine to the double bonds competes with a slow substitution reaction. The iodine titration value at 1 hr. was however a measure of relative unsaturation.[29,121]

2.5.2 Monounsaturation

The acetic acid liberation method of Martin[123] was employed for determining monounsaturation.

0.5g of powdered polymer was swollen in 75 ml of chloroform for 12 hr. in a conical flask fitted with a rubber seal. 4g of acid-free mercuric acetate and 30 ml of methanol were added. 75ml of saturated aq.NaCl and 100 ml of distilled water were added. The liberated acetic acid was titrated with 0.1N NaOH after 3 hr. and the phenolphthalein end point was determined. Blank runs were determined for each set of experiments and the results were suitably corrected.

2.5.3 Total Colour Difference

Colour formation in compression moulded films was expressed as the total colour difference relative to the calibrated standard films moulded under similar conditions but which had not undergone processing at 180°C. Measurement was carried out using the MEECO Colourmaster Model V in transmission. Readings were obtained using red, green and blue filters and the total colour difference ΔT was calculated by means of the formula[121] (2):

$$\Delta T = (\Delta R^2 + \Delta G^2 + \Delta B^2)^{1/2} \qquad (2)$$

where ΔR, ΔG and ΔB are the differences between the instrument readings of the test sample and the standard sample using the red, green and blue filters respectively.

2.5.4 Gel Content

0.5g of powdered polymer was refluxed for 10 min. with 50 ml of AR dichloromethane. Two aliquot portions of 25 ml of the suspension were centrifuged in capped polypropylene tubes for 30 min. at 15000 rpm. The clear solution was decanted and the gel was washed with fresh solvent followed by recentrifugation. The gel was dried overnight at room temperature and then vacuum dried to constant weight.

2.5.5 Peroxide

0.5g of powdered polymer was swollen in 75 ml of deaerated chloroform for 12 hr. in a conical flask fitted with a rubber seal. 1 ml of deaerated glacial acetic acid was added, followed by 25 ml of freshly prepared 5% NaI. After allowing to stand for 4 hr. in the dark at room temperature, the liberated iodine was titrated with 0.1N $Na_2S_2O_3$.

For each set of experiments, blank titrations were run and test results were suitably adjusted. The reactions involved in this process are as shown (3,4)

$$ROOH + 2I^- + 2H^+ \longrightarrow ROH + H_2O + I_2 \qquad (3)$$

$$2S_2O_3^{2-} + I_2 \longrightarrow 2I^- + S_4O_6^{2-} \qquad (4)$$

2.6 Infrared Spectrophotometric Measurements

2.6.1 Determination of Carbonyl Formation

Infra-red spectrophotometry was used to monitor the formation of carbonyl moiety. The concentration of the carbonyl group was expressed as an index defined as the ratio of the absorbance of the carbonyl at 1725 cm^{-1} relative to the polymer reference peak at 2915 cm^{-1}. The latter peak due to C-H bond stretching did not undergo any appreciable change during long-time monitoring, hence its use as an internal reference peak. Transmittance values read off from the infra-red chart paper were converted to absorbance values using a reckoner conversion chart supplied by Perkin-Elmer. Indices are reported as $A1725cm^{-1}/A2915cm^{-1}$.

2.6.2. Determination of Hydroxyl Formation

The formation of hydroxyl groups in PVC was monitored by the infra-red absorption at $3450cm^{-1}$. The concentration of hydroxyl group was also expressed as an index relative to the peak at $2915cm^{-1}$ ie. $A3450cm^{-1}/A2915cm^{-1}$.

2.6.3. Measurement of Other Chemical Species

The changes in unsaturation of PVC during processing were monitored by uv absorption maxima at 230, 275, 310 and 365nm. The olefinic C-H index was monitored by infra-red index A2850cm^{-1}/A2915cm^{-1}, this mono-unsaturation was responsible for the U.V. absorption at 230 nm. The other U.V. absorption maxima at 275, 310 and 365 nm arise from poly-conjugated structures in PVC.

The decay of the carboxylate infra-red absorbance at 1575-85cm^{-1} in PVC stabilised with DBTM was monitored as an index by i.r. Similarly, formation of the ester group in PVC was measured by the carbonyl index A1730cm^{-1}/A2915cm^{-1}. The development of the evolved maleic anhydride from the reaction of DBTM was also measured as A1780cm^{-1}/A2915cm^{-1}.

2.7 Electron Spin Resonance (ESR) Spectroscopy

2.7.1 The Principle of E.S.R. Spectroscopy

An unpaired electron, as in a free radical, has magnetic properties due to the intrinsic angular momentum known as the electron spin. The unpaired electron is a magnetic dipole as a result of the spinning motion of the electric charge. The intrinsic angular momentum of the electron is known as the spin vector (S). The magnetic moment of the unbonded electron (μe) is related to the spin vector by (5)

$$\mu e = - ge\,\beta eS \quad (\text{erg } G^{-1}) \qquad (5)$$

where g is the dimensionless constant called "the Lande g-factor" or "electron free-spin g factor" ($g = 2.\ 23$), βe is the "Bohr Magneton" the negative sign indicates that the vector of the magnetic moment (μe) of the electron is in opposite direction to the spin vector (S).

2.7.2 The Resonance Condition

When an electron is in a magnetic field (H), its magnetic moment vector has two permissible states corresponding to its magnetic moment being alligned in either the same or opposite direction to the applied external field. These two orientations are parallel and antiparallel to the applied magnetic field. The electron energy (E) in the magnetic field (H) is given by (6)

$$E = - \mu eH \text{ (erg)} \qquad (6)$$

Substituting equation (5) into equation (6) gives

$$E = g_e \beta_e SH \text{ (erg)} \qquad (7)$$

The spin quantum number Ms of an electron is $^1/2$; the spin vector (S) in a magnetic field can have one of the two possible values +1/2 and -1/2. Hence the energy of an electron is a magnetic field (H) is either

$$E_1 = + 1/2\ g_e\ \beta e\ H \qquad \text{or } E_2 = -1/2\ g_e \beta eH \qquad (8)$$

The energy difference between the two states of the electron in a magnetic field H is given by

$$\Delta E = E_1 - E_2 = g_e \beta eH \qquad (9)$$

The measurement of the energy difference (ΔE) is the basis of electron spin resonance (esr) experiments (fig. 2.1).

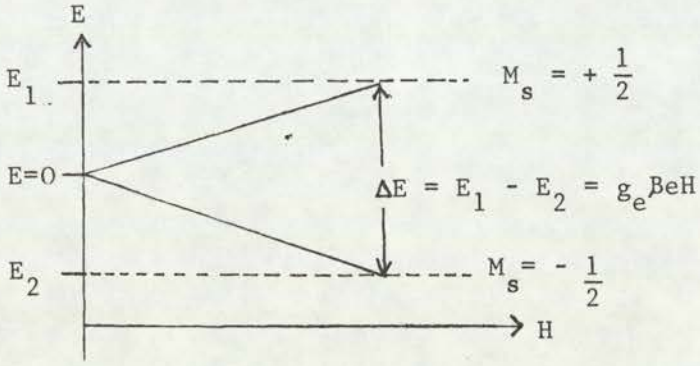


Fig. 2.1 Energy level diagram showing Zeeman splitting for a free electron.

In the absence of a magnetic field, the two energy levels E_1 and E_2 are degenerate. The increase of the number of energy levels of an electron by application of an external magnetic field is called "the Zeeman splitting of the electron". This phenomenon removes the degeneracy of the system giving the distinct energy levels as shown in fig. 2.1.

Transitions between the levels can be induced by irradiating the sample with electromagnetic radiation of a frequency such that the energy of the radiation is precisely the same as the energy difference between the levels. Hence, application of an oscillating radio frequency field perpendicular to the magnetic field (H), whose energy quanta (hv) equal to $g_e \beta e H$ induces transition between the two energy states of the electron, the fundamental equation of e.s.r. spectroscopy being (10)

$$h\nu = \Delta E = E_1 - E_2 = g_e \beta e H \qquad (10)$$

where v is the frequency of the radio waves (cycles S^{-1}). Under such conditions, resonance occurs and electrons in the lower level absorb energy from the incident radiation and are excited into the upper level, while electrons in the upper level emit energy and fall back to the lower level. Thermal equilibrium with the surroundings involves having more electrons in the lower level than in the excited state and absorption of radiation occurs slightly more frequently than stimulated emission. The overall result is that there is a net absorption of energy from the incident radiation, and it is this loss of incident radiation that is detected, amplified and displayed by the spectrometer. All e.s.r. experiments in this work were done on a JEOL-PE spectrometer.

2.7.3 The g-value

The line position of an esr spectrum is measured by the g-value as the ratio of the microwave frequency to the external magnetic field at resonance (11).

$$g_e = \left(\frac{h}{\beta_e}\right) \cdot \frac{\nu}{H} \qquad (11)$$

The g_e value of a free electron is 2.0023, whereas the g-values for free radicals in atoms, molecules, and crystals depend on their electronic structure.

The application of a double cavity in the esr apparatus simplifies the measurement of g-values. Special standard compounds with precisely determined g-values are used as reference. These standard compounds are inserted into the double-channel recorder. The separation of the centers of the two spectra represents the magnetic field difference at the two positions of the sample. One of the standard samples is replaced by a sample to be examined and the magnetic field difference (ΔH) between the centres of the esr spectra is measured. The g-value of the unknown sample (gu) can then be calculated from the equation (12):

$$g_u = g_s - \left(\frac{\Delta H}{H}\right) g_s \qquad (12)$$

where g_s is the g-value of the known standard sample and H is the applied external magnetic field. In this work, the manganese reference marker (standard) was used for the measurement of g-values. The Mn^{2+} ion gives an esr spectrum of six lines and a g-value of 1.981 which does not vary significantly between the frequency range 9200 to 9400 Hz. Therefore all measurements were made using electromagnetic radiation of 9300Hz microwave frequency.

2.7.4 Concentration of Free Radicals

The integrated intensity of the esr signal represents the total energy absorbed by the sample at resonance conditions. This intensity is expressed by the total area under the resonance curve and it can be used for the determination of the relative concentration of free radicals in the sample as the number of unpaired spins per gram, per millilitre, or per millimetre length of sample. The intensity of the esr spectra is influenced by several experimental factors such as the transition probability, the microwave frequency, the modulation aplitude at the sample, the concentration of free radicals in the sample, the g-value of the sample and the sample temperature. Since many factors influence the intensity of esr signal, the absolute determination of free radical concentration involves many errors and consequently requires many corrections, and it is carried out very rarely.

The usual method of measuring the concentration of free radicals in an unknown sample is to compare its esr signal with that of a sample containing a known quantity of free radicals[124].

The relative concentration of free radicals in PVC samples were obtained by using a reference sample in the cavity together with test samples so that both spectra are recorded simultaneously. For this purpose, a sealed capillary tube containing 10mg of 0.1M $CuSO_4$ solution was fastened to the outer surface of the glass tube in which the PVC sample was placed. The relative radical concentration of the test PVC sample was calculated according to the equation[124] (12).

$$\text{Concentration of radical in test sample} = \frac{Y'm\,(\Delta Hpp)^2\ \text{sample}}{Y'm(\Delta Hpp)2\ \text{reference}} \times \text{concentration of radical in reference sample} \qquad (12)$$

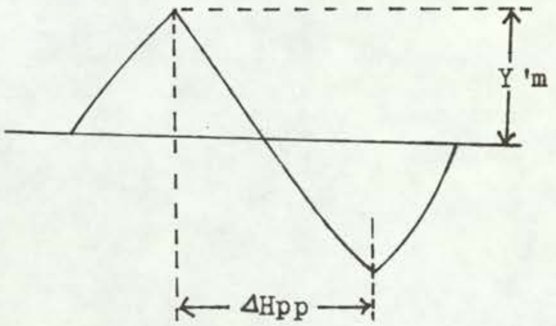


Fig. 2.2 **Relative concentration of free radicals in esr spectra.**

CHAPTER III

PHYSICAL AND CHEMICAL CHANGES IN PVC DURING THERMAL PROCESSING

3.1 Experimental Procedure

PVC samples were processed alone or in the presence of DBTM and a synergistic lubricant system consisting of 0.65% Wax E and 0.8% CaSt for various periods at 180°. Some experiments were performed at other temperatures for the purpose of comparing them with the effects at 180°C at which temperature most of the present work were done. Detailed experimental procedures and instrumentations were described in Chapter 2.

3.2 Results

Mechanochemical degradation of PVC during processing in a RAPRA torque rheometer at 180°C was monitored by measuring the shearing forces operating on the polymer as measured by the applied torque, fig. 3.1. The initial torque fell very sharply to a minimum level and this was followed shortly by a transient small peak centred around 1 min. of processing which subsequently decayed. This was followed by a short equilibration period which is often referred to as the "stabilisation period". An upward inflexion in torque was then observed signifying onset of crosslinking in the resin which preceded a final fall in the torque level. The decrease in torque demonstrates chain-fragmentation reactions which in effect lead to molecular weight

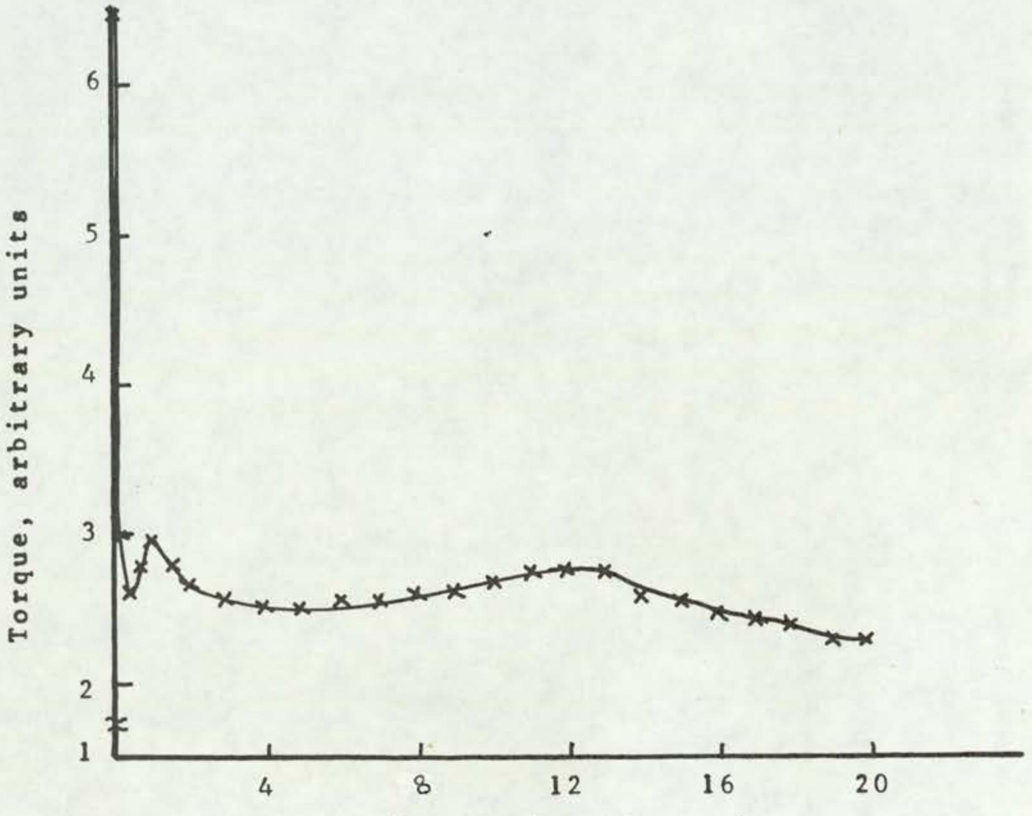


Fig. 3.1: Changes in the melt viscosity of unstabilised PVC during thermal processing at 180°C as monitored by the torque.

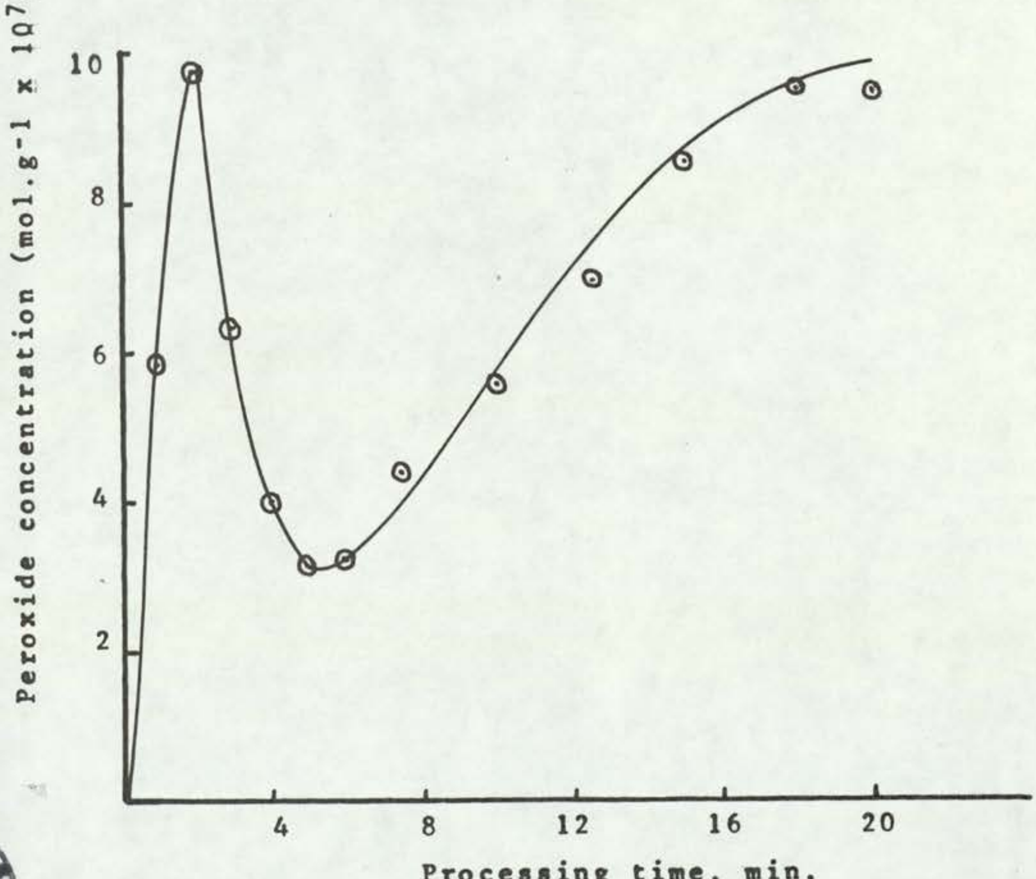


Fig. 3.2: Effect of thermal processing at 180°C on peroxide concentration in unstabilised PVC

reduction in the polymer. This is an evidence of extensive damage to polymer chains under prolonged thermal processing.

Figure 3.2 shows the effect of processing time on peroxide concentration in unstabilised (control) sample of PVC. A rapid accumulation of peroxides was observed in the first two minutes of processing, followed by a rapid decay to a minimum level and then a second increase. Gel formation (fraction of polymer which is insoluble in dichloromethane) in the polymer during processing, fig. 3.3, follows a strikingly similar trend to peroxide concentration (fig. 3.2). The nature of the peroxides formed in the early stages of processing was shown earlier[27,28,121] to be partially in the form of crosslinks between polymer molecules which manifested in the form of solvent insoluble gel. The present results (figs. 3.1-3) agree with the work of Vyvoda[121] and the similiarity between the peroxide and gel (figs. 3.2 and 3) demonstrates the formation of macroalkyl peroxyl linkages in PVC during mechanochemical degradation.

Figure 3.4 shows the development of olefinic unsaturation in unstabilised PVC measured by the i.r. absorption peak at $2850cm^{-1}$. An initial rapid growth is followed by a linear rate of increase in unsaturation with increasing processing time. A similar curve was obtained for chemically measured unsaturation, fig. 3.5. The rate of formation of colour by colourimeter (Colourmaster Model V), is shown in fig. 3.6. Similarly, a two-stage development of colour is noticed, an initial auto-catalytic accumulation of colour is followed by a rather linear increase of colour formation. These results suggest a change

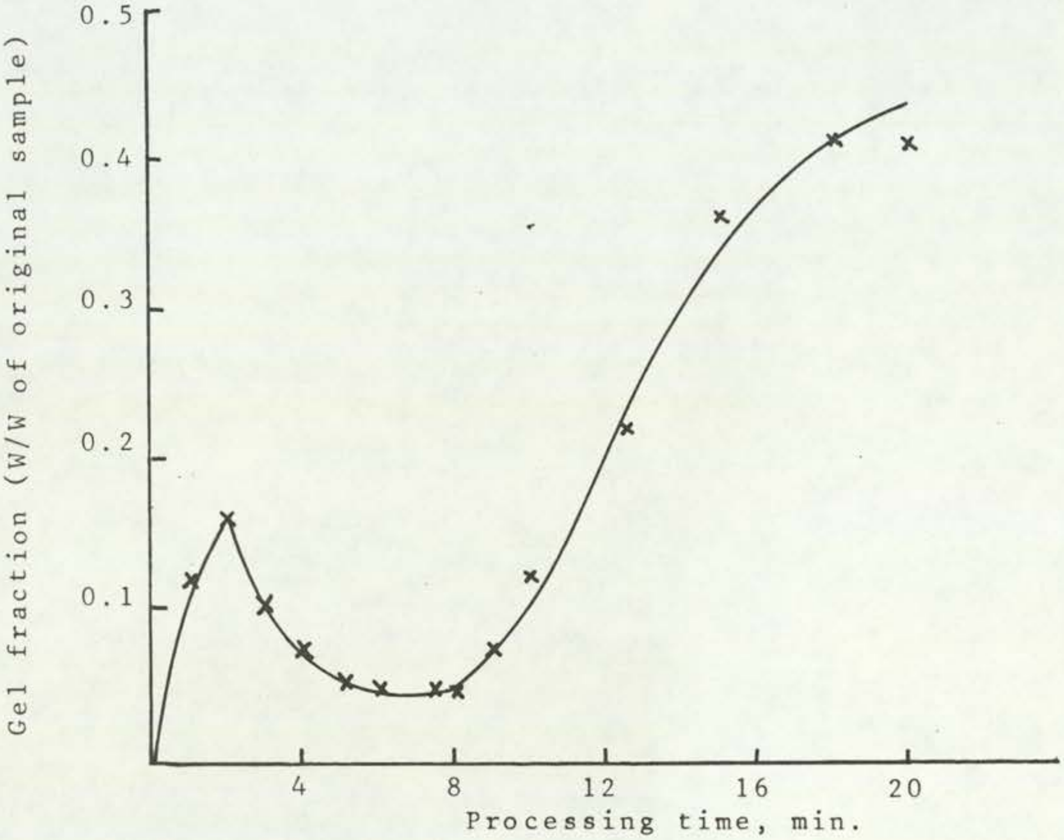


Fig. 3.3: Effect on thermal processing at 180°C on gel formation in unstabilised PVC.

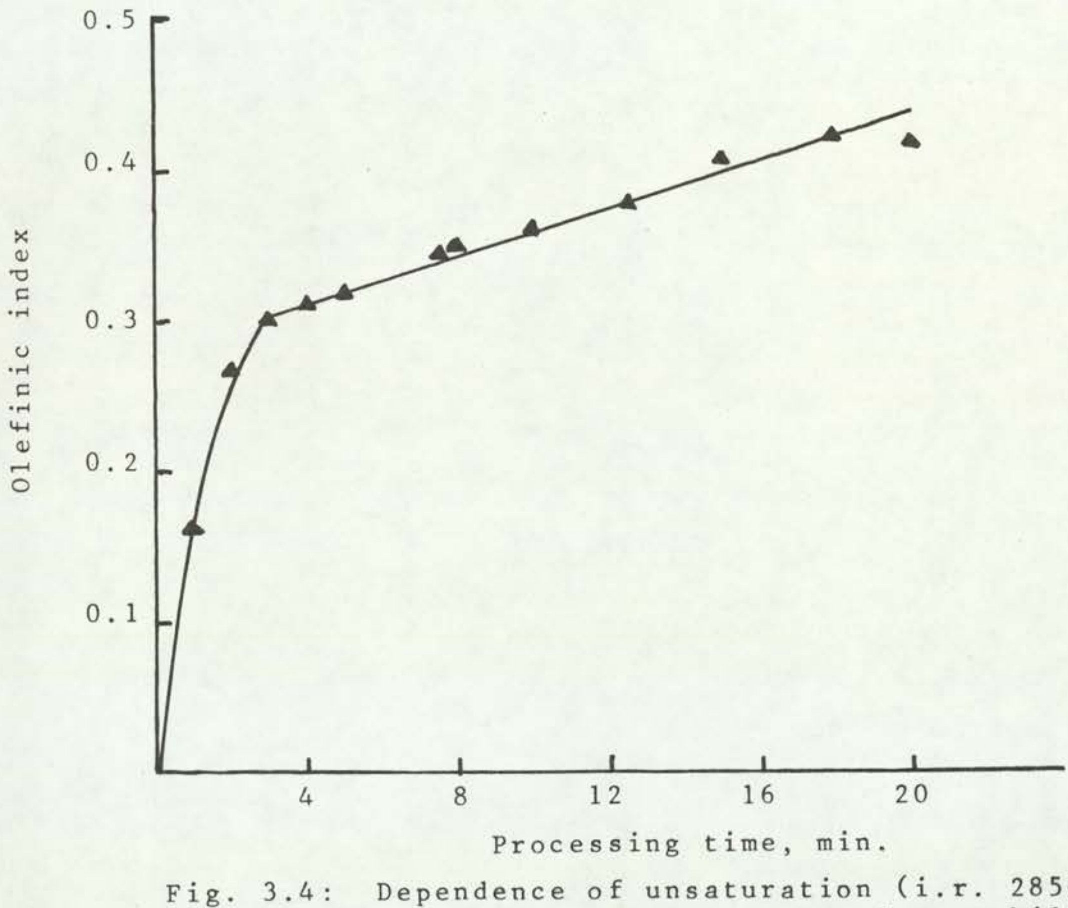


Fig. 3.4: Dependence of unsaturation (i.r. 2850 cm^{-1}) in CH_2Cl_2- soluble phase of unstabilised PVC on thermal processing at 180°C.

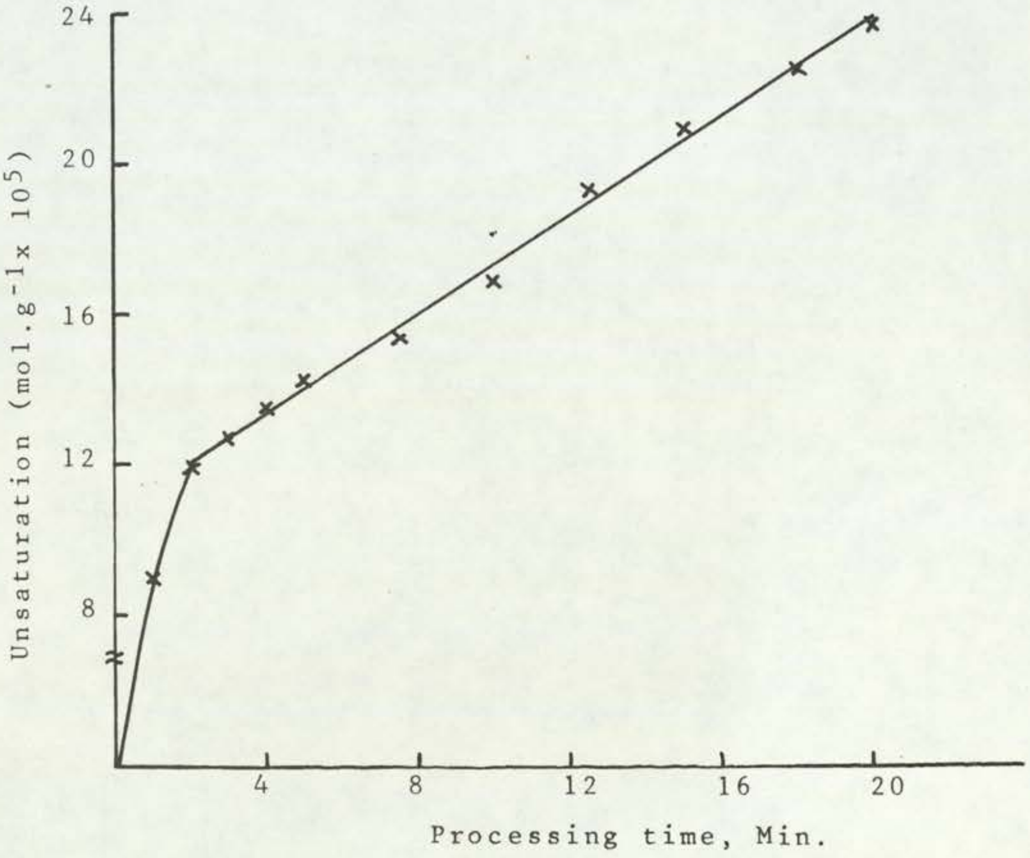


Fig. 3.5: Effect of thermal processing at 180°C on formation of unsaturation in unstabilised PVC.

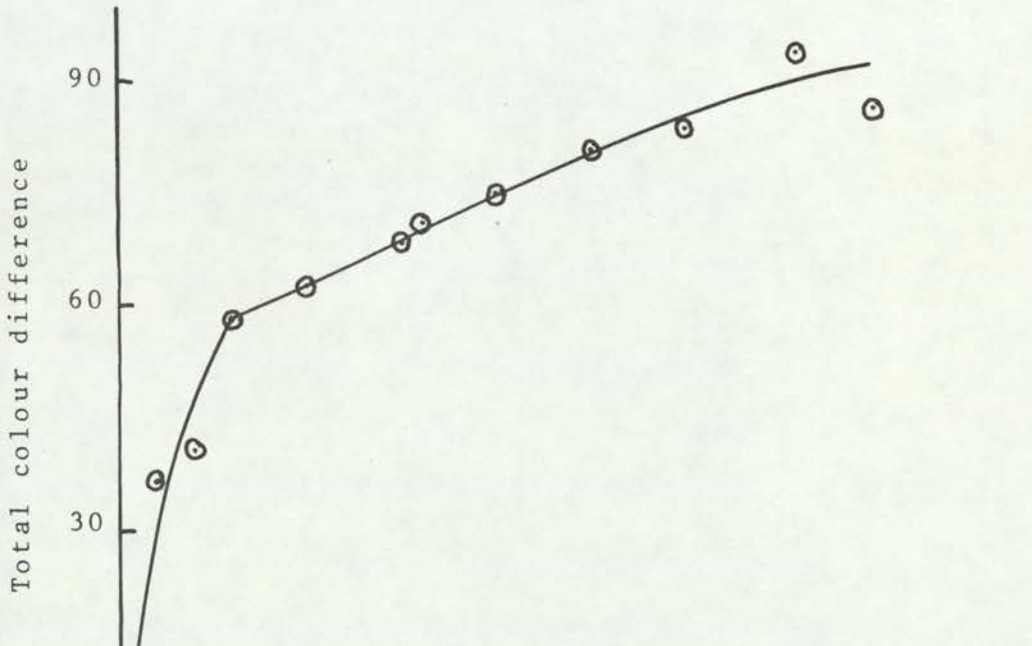
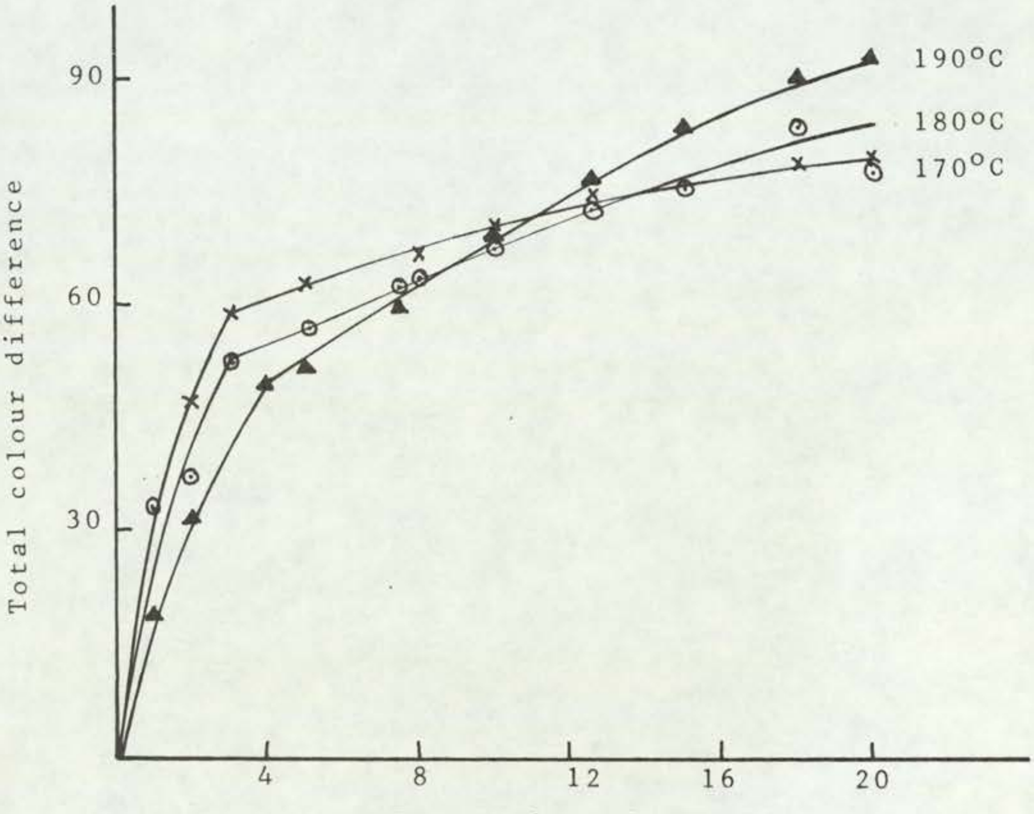


Fig. 3.6: Effect on thermal processing at 180°C on colour formation in unstabilised PVC.

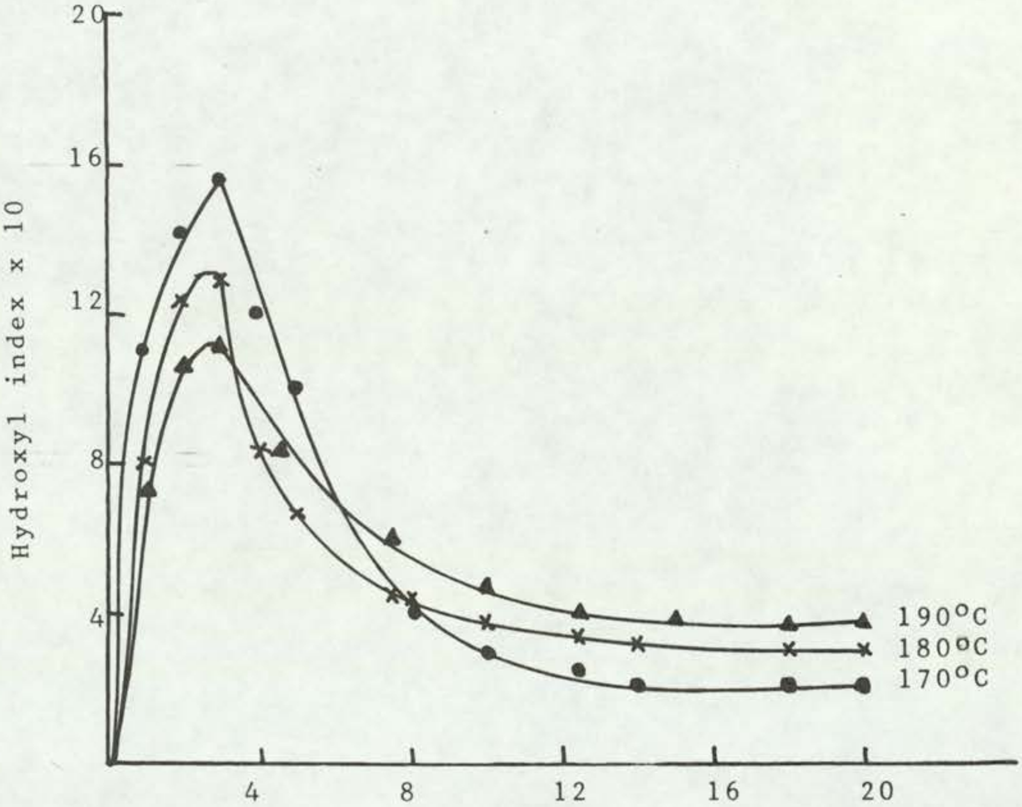
from the predominant effect of mechanical shear in the first part of processing to the predominance of thermal degradation in the second stage of processing.

The rates of colour formation at 170, 180 and 190°C are compared in fig. 3.7. It is noticed that total colour formation increases with increasing processing temperature. The dependence of the hydroxyl index of hydroperoxides formed during the processing of unstabilised PVC at various temperatures is shown in fig. 3.8. In the early stages of processing, hydroxyl index is found to be inversely proportional to temperature while a crossover occurs at higher processing times when the hydroxyl index becomes proportional to temperature. This effect indicates that the shearing forces operating on the polymer chains in the early stage of processing are severest at 170°C and least at 190°C whereas at longer processing times the effects of thermal degradation are most severe at 190°C and least at 170°C. The relationship between the i.r. olefinic index and chemically determined unsaturation in PVC during thermal processing is shown in fig. 3.9. The corresponding relationships between olefinic index and total colour difference and between unsaturation and total colour difference are shown in fig. 3.10 and 11 respectively. Although no linear relationship between these functional groups measured by the different methods is established, the similarity between the curves (figs. 3.9-11) demonstrates however a consistency in the relative measurements of the concentration of the functional groups.



Processing time, Min.

Fig. 3.7: Effect of processing temperature on colour formation in unstabilised PVC.



Processing time, Min.

Fig. 3.8: Effect of processing temperature on the hydroxyl group (i.r. 3450 cm^{-1}) of the dichloromethane-insoluble phase in unstabilised PVC.

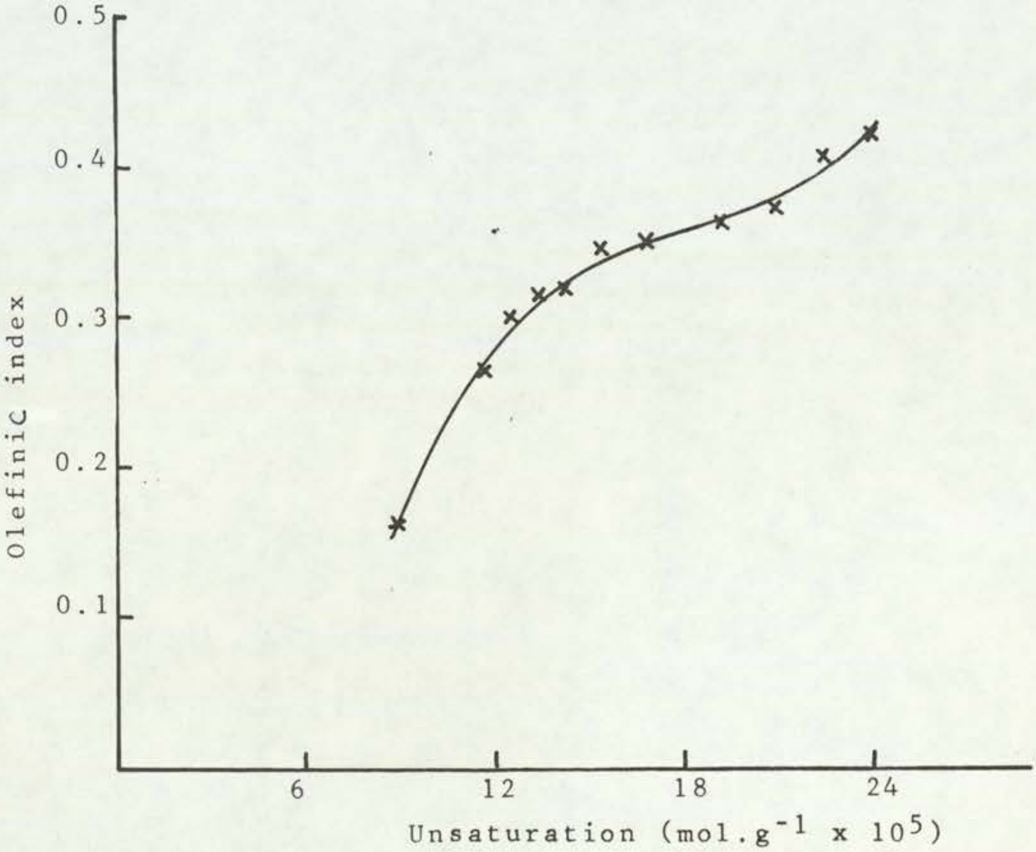


Fig. 3.9: Relationship between i.r. olefinic index and chemically measured unsaturation in PVC.

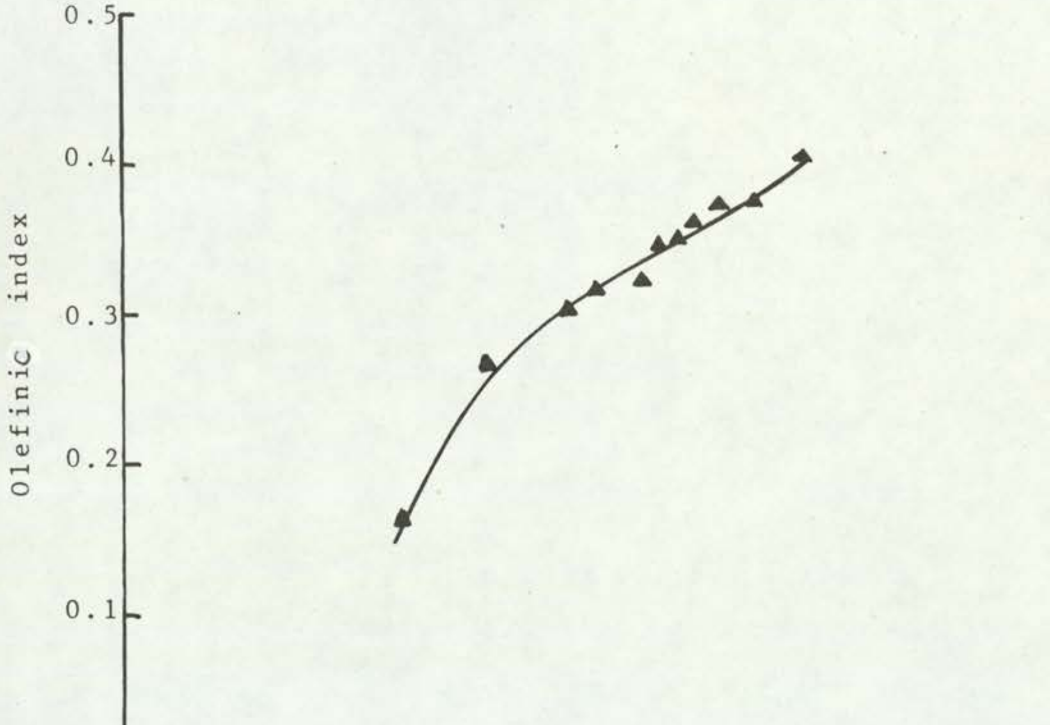


Fig. 3.10: Relationship between i.r. olefinic index and total colour difference measured by MEECO Colormaster Model V.

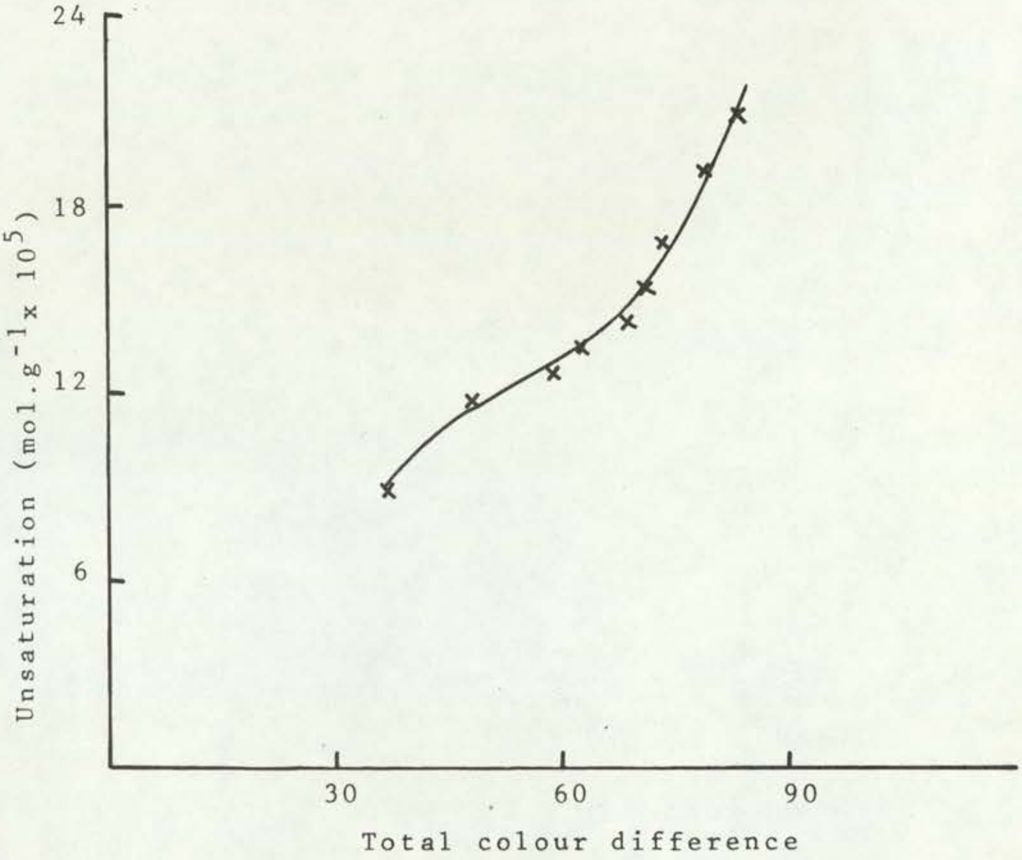


Fig. 3.11: Relationship between chemically measured unsaturation and total colour difference measured by MEECO Colormaster Model V.

3.2.1 Effect of Lubricants and Stabiliser

PVC was formulated with 0.65% Wax E, 0.8% CaSt and 2.5% DBTM and processed at 180°C. A synergistic lubricant system consisting of both Wax E and CaSt was also processed and the formulations were compared with the control sample without additive.

For all processed formulations, the control sample without additive exhibits the highest initial torque level as shown in fig. 3.12. One effect of the incorporated additives is to lubricate and/or plasticise the rigid polymer. This effect softens the polymer and reduces the mechanical work required for processing as measured by the torque. The role of the commercial lubricant Wax E, which is a conventional "external" lubricant is to "wet" the surface of the rheometer chamber and the contacting surfaces of the polymer.[37,125] In this way, it produces an interface with lower friction between the metal and the polymer. Consequently, this reduces local overheating and charring of the resin. The effect of the internal lubricant CaSt, is to act within the polymeric material itself by reducing the cohesive forces at the molecular interfaces. Although lubricants are conventionally classified as either external or internal, however, their roles under commercial and technological processing conditions cannot be so specifically restricted. Moreover, lubricants impart some stabilising effect by prolonging the time to onset of thermal degradation arising possibly from the reduction of the powerful shearing forces operating on the polymer chain in the first minutes of thermo-mechanical processing of the polymer.[27,28]

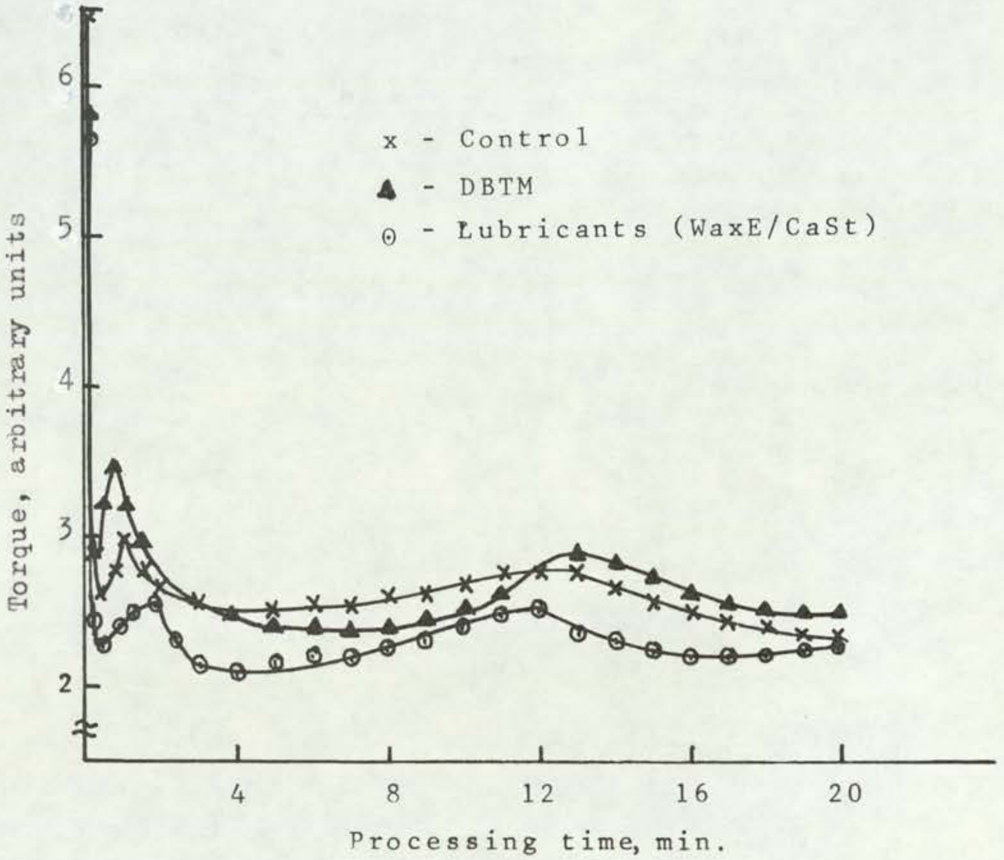


Fig. 3.12(a): Effect of DBTM and CaSt on the torque generated inPVC during thermal processing at 180°C.

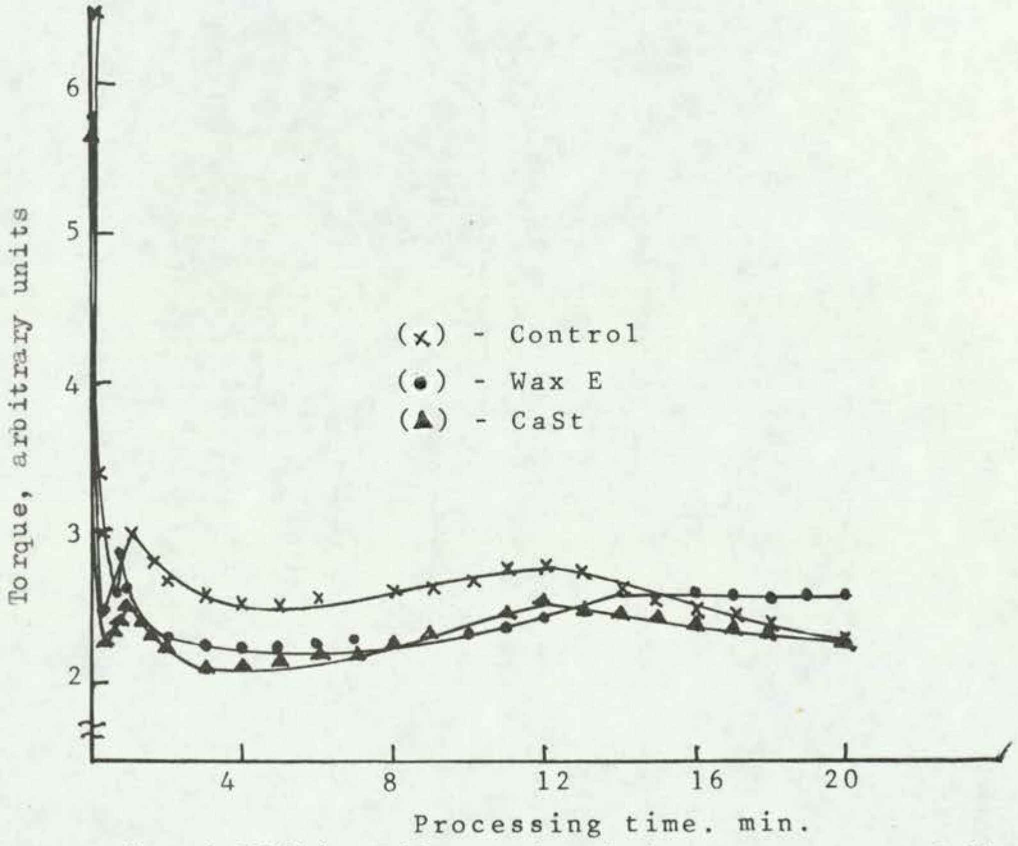
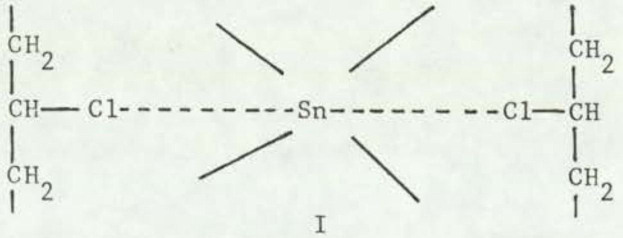


Fig. 3.12(b): Effect of calcium stearate and Wax E on the torque generated in PVC during thermal processing at 180°C

A comparison of the lubrication effectiveness of Wax E, CaSt and DBTM in reducing the shearing forces on the polymer chain in the early stage of processing as deduced from the torque indicates the following order: CaSt > Wax E > DBTM. In all stabilised formulations of PVC, the highest values of torque are obtained in the presence of DBTM. Similar observations were previously reported by Vyvoda[121]. High levels of torque in the presence of this tin-based stabiliser may be caused by the tendency of the tin metal atom of the stabiliser to satisfy its vacant d-orbital requirements with the p electrons of the pendant chlorine atoms on the polymer chain.[21] In this way, secondary "dative" structures may be set up which tend to increase the apparent density and rigidity of the polymer and hence increase the dynamic inertia or stiffness of the formulation. An invokation of the vacant d-orbital requirements of the metal stabiliser giving rise to increased torque or melt viscosity as a result of intermolecular chain association may, perhaps, not completely exonerate calcium from behaving differently than tin. However, it must be recognised that the organotin metal has a hexacoordinate aptitute while group II metals to which class calcium belongs have tetracoordinate aptitutes.

The probable intermolecular linkages between tin stabiliser and PVC molecules are as shown (I).[21]



I

This phenomenon causes a "densification" of the polymer molecules and increases the rigidity of the composition. All other conditions of processing being equal, the rate of shear-induced mechanical chain rupture will be determined by the interaction forces and strengths of the chemical bonds of the polymer molecules, and, consequently, the extent of chain rupture on this account is higher for polymers with strong intermolecular interactions. As such, formation of I would lead to high torque as was indeed found with DBTM formulations (Fig. 3.12a). The formation of a complex similar to I was proposed previously[21] to explain the mechanism of stabilisation of PVC afforded by organotin compounds and other metal salts. It was suggested that one (or possibly two) of the chlorine atoms on the polymer chain forms a dative bond with the tin atom in which such a complex serves as a precursor by means of whih the displacement of relatively labile halogen atoms can be effected.[21] Evidence in support of such coordinative organotin complexes was also given by other workers.[126] However, the formation of such an associated complex was proposed[21] without any consideration of the consequence of such structures on the dynamic processibility as is demonstrated by torque (fig. 3.12a) and by previous work.[27,28]

The dichloromethane- insoluble fraction in PVC during processing in the absence and presence of DBTM and the synergistic lubricant mixture of Wax E and CaSt are compared in fig. 3.13. The gel fraction is reduced in the presence of lubricants than the control sample but the shape of the curves is similar and both show a two-stage formation of gel. In the presence of DBTM, the first stage gel peak was smallest and the second stage growth was eliminated. The dependence of gel fraction on DBTM concentration is shown in fig. 3.14.

It is seen that the induction period increases with increasing DBTM concentration (see fig. 3.14 (curves c-e)). The peroxide concentration in the absence and presence of DBTM and lubricants is shown in fig. 3.15. Again, the lubricants reduce formation of peroxides compared with the control sample but the shape of the curves is very similar. In the presence of lubricants and 7.2×10^{-3} mole % DBTM, the initial peroxide concentration is substantially reduced with no further increase at longer processing times up to 20 min. Figure 3.16 shows the dependence of peroxide concentration on DBTM concentration. At 5.8×10^{-3} mole % DBTM an induction period of 12 min. was obtained for the formation of second stage peroxides whereas at 2.9×10^{-3} mole % DBTM, the second stage peroxides appear after about 8 min. and the shape of the curve is also similar to samples containing the lubricants alone.

The olefinic index of the i.r. unsaturation ($2850 cm^{-1}$) in the presence of lubricants and is compared with the control sample in figs. 3.17 and 18. An initial rapid rate of formation of unsaturation is followed by a lower linear rate of increase in both the control and lubricants-formulated samples. Further growth of unsaturation is prevented beyond 2 min. of processing in the presence of 7.2×10^{-3} mole % DBTM. At 5.8×10^{-3} mole % DBTM, a further increase in unsaturation is noticeable after 12 min while at 2.9×10^{-3} mole % DBTM, the induction period to further increase in unsaturation

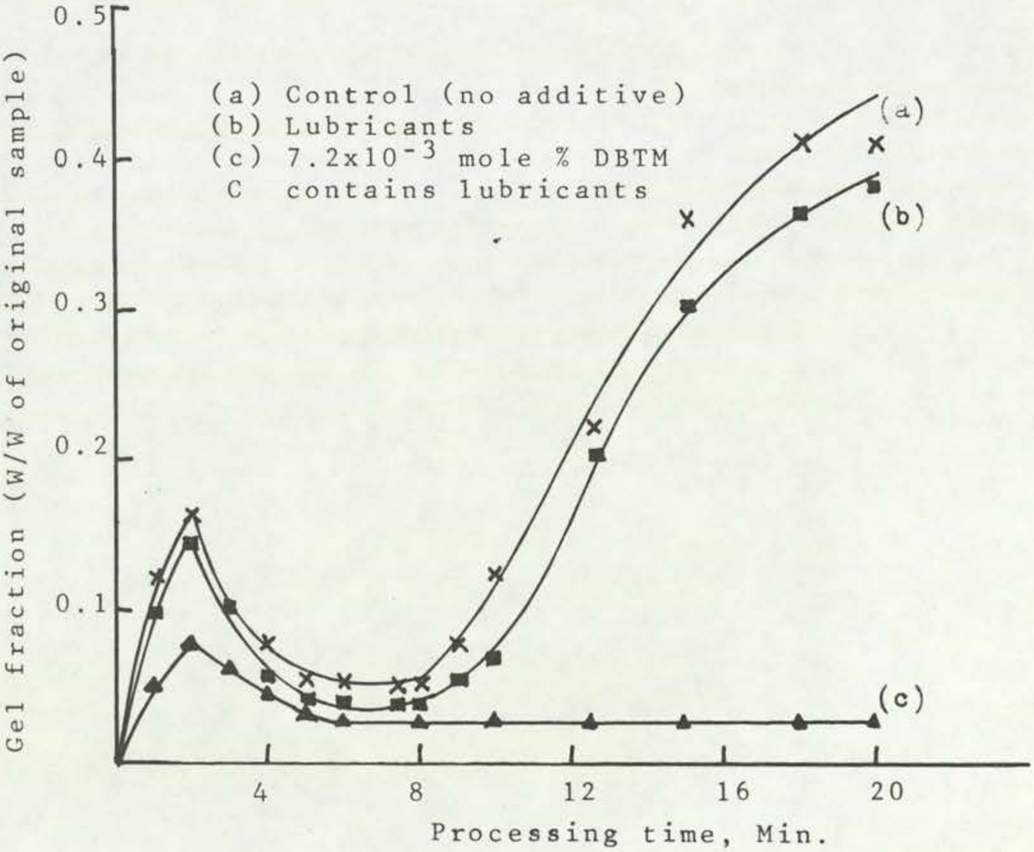


Fig. 3.13: Effect of thermal processing at 180°C on gel formation in unstabilised PVC.

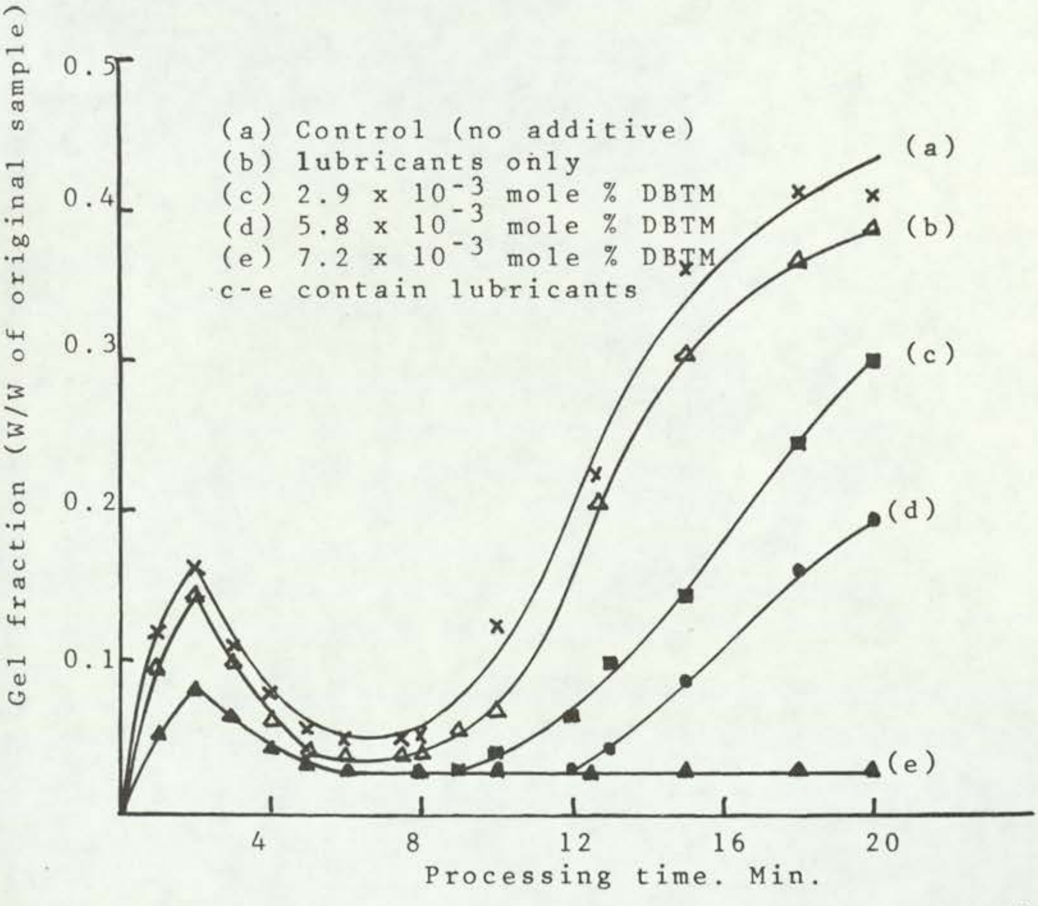


Fig. 3.14: Effect of thermal processing at 180°C on gel formation in PVC: dependence on DBTM concentration

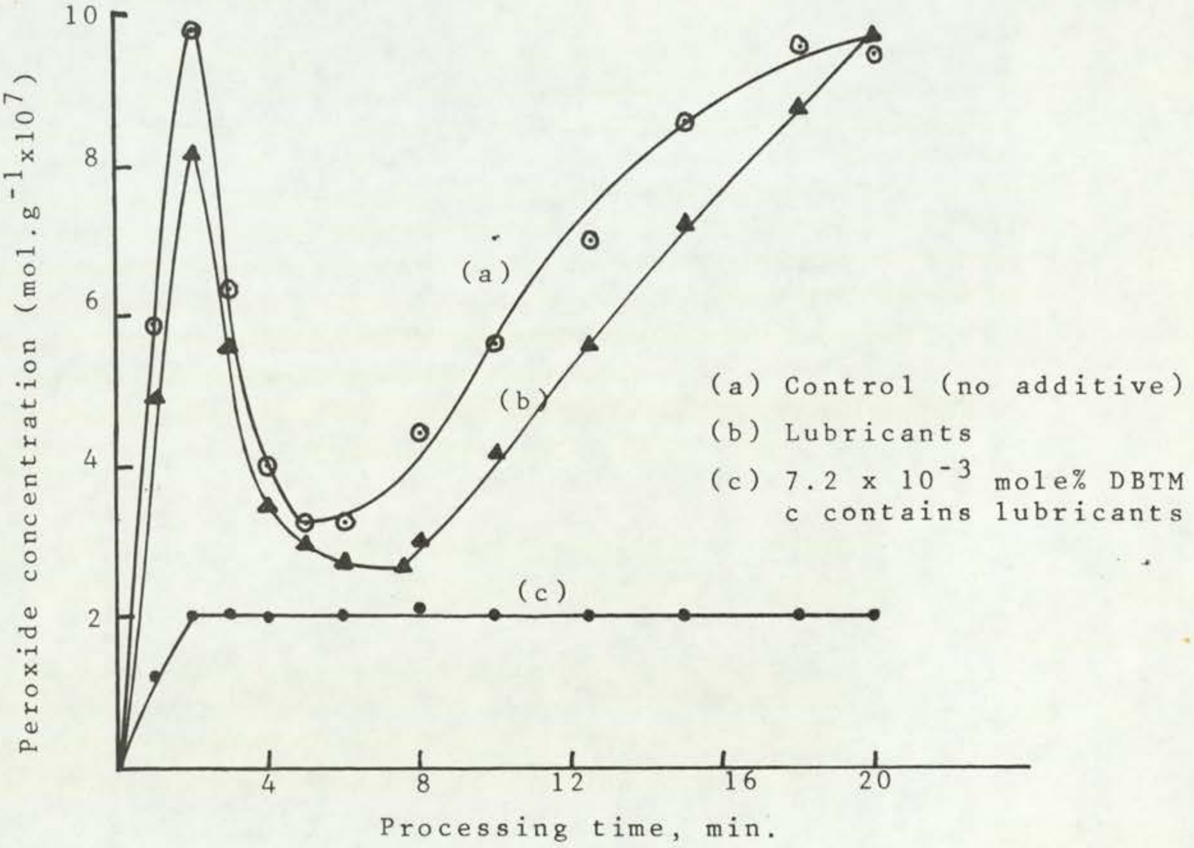


Fig. 3.15: Effect of thermal processing at 180°C on peroxide concentration in PVC.

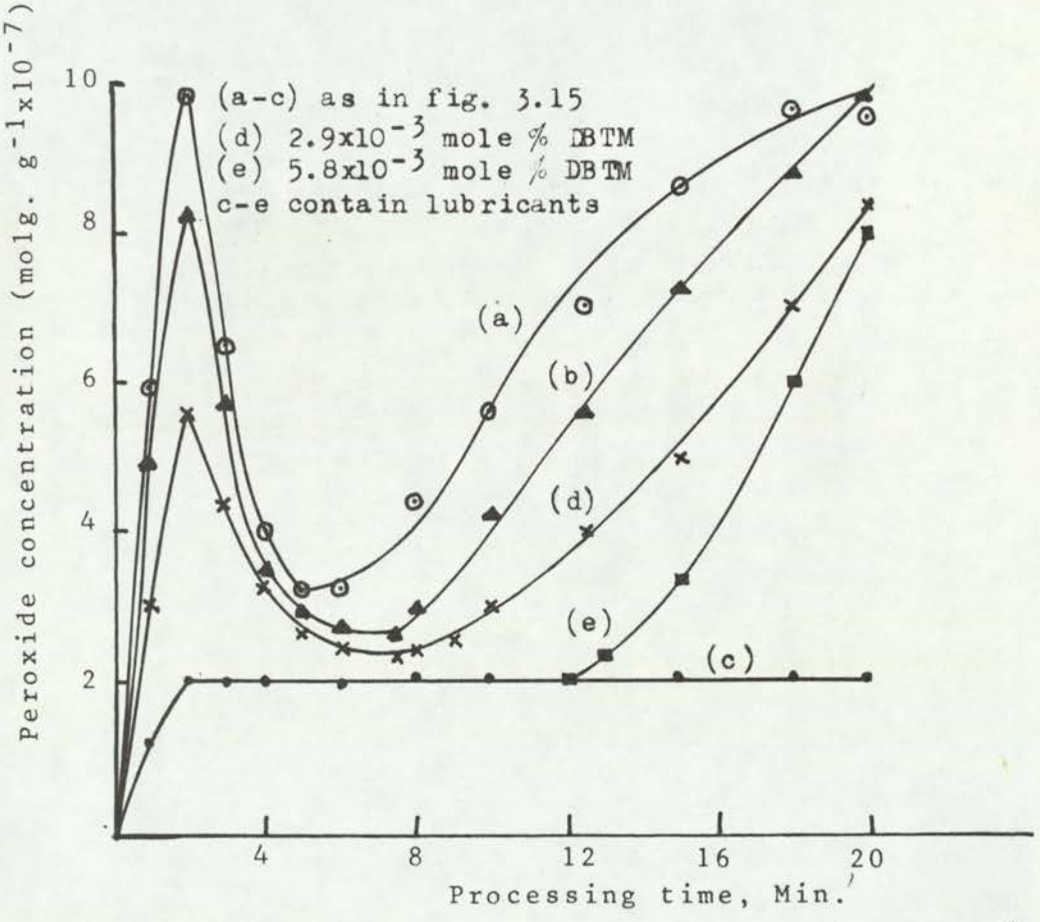


Fig. 3.16: Effect on thermal processing at 180°C on peroxide concentration in PVC: dependence on DBTM concentration

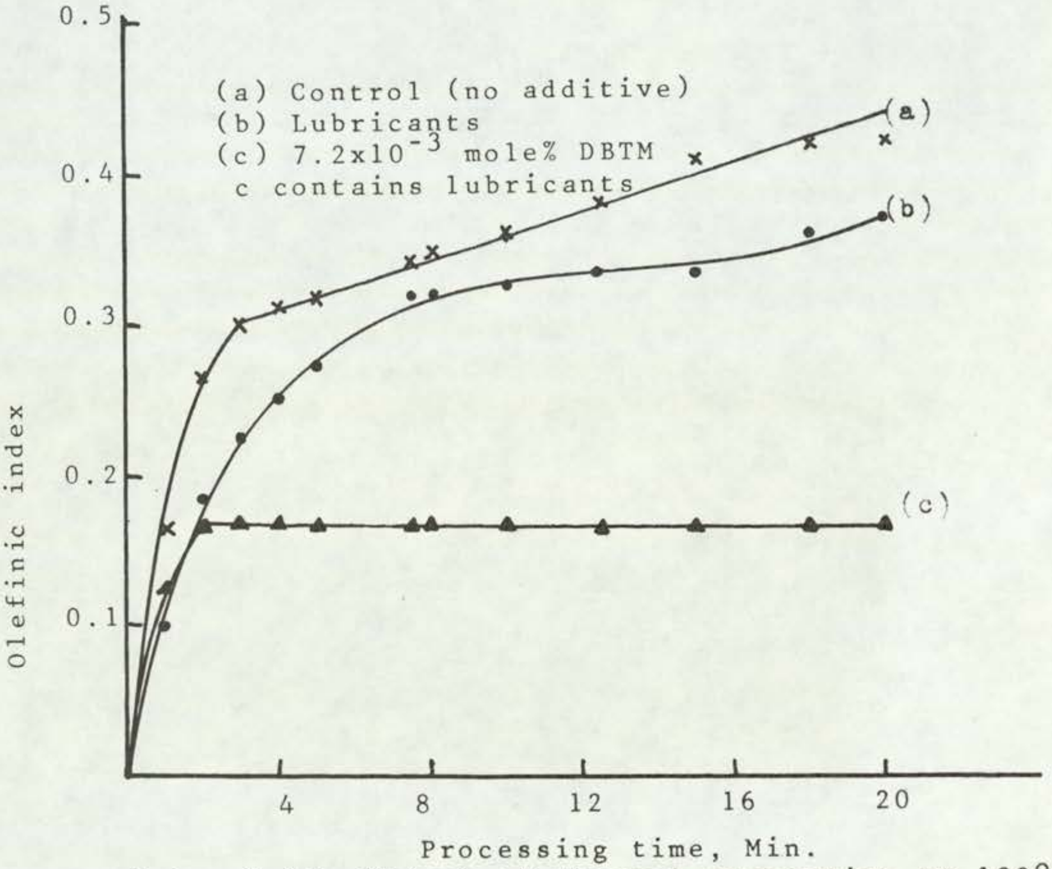


Fig. 3.17: Effect of thermal processing at 180°C on unsaturation (i.r. 2850 cm^{-1}) in PVC.

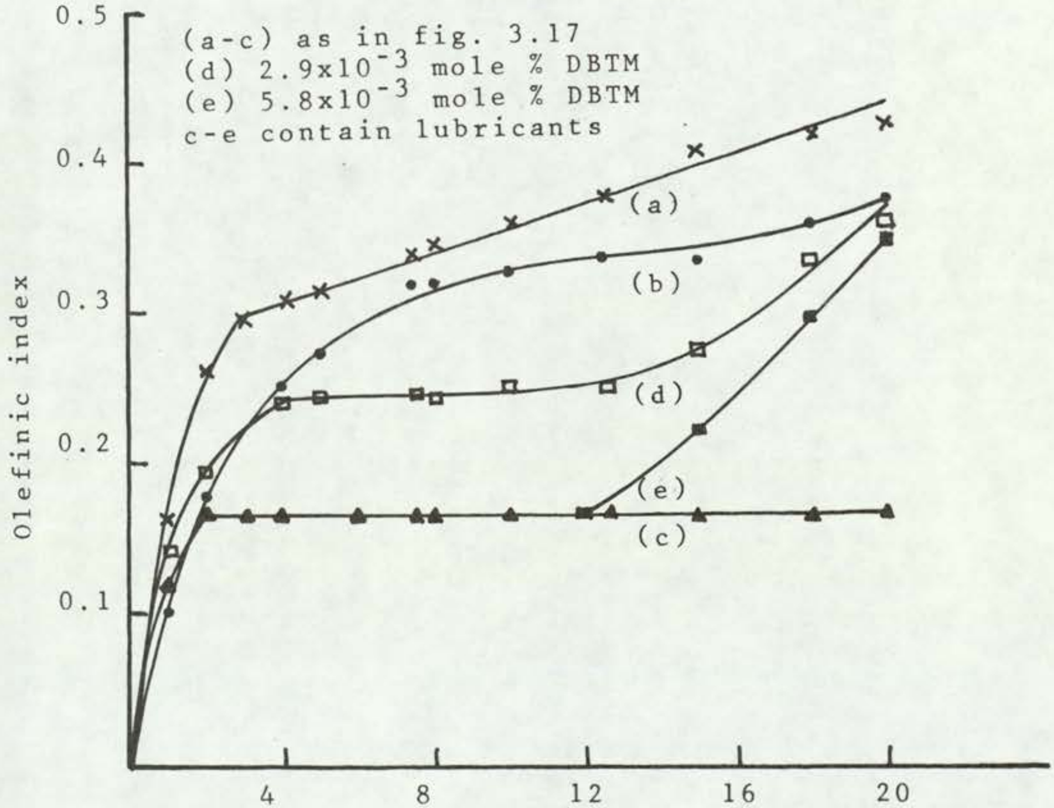


Fig. 3.18: Effect of thermal processing at 180°C on unsaturation (i.r. 2850 cm^{-1}) in PVC: dependence of DBTM concentration.

is reduced to about 8 min. A similar behaviour to the i.r. index was obtained with chemically determined unsaturation in PVC during the processing operation, figs. 3.19 and 20. The effect of thermal processing in the absence and presence of lubricants and DBTM on total colour difference in PVC is shown in fig. 3.21 while fig. 3.22 shows the dependence of colour on DBTM concentration. The similarity between the i.r. index of unsaturation, the chemically determined unsaturation and the colourimetric measurement is evident. A similar relationship was also found for these measurements in the control sample (see figs. 3.9-11).

3.2.2 Molecular Weight Changes in PVC

The changes in molecular weight and molecular weight distribution of the fraction of the polymer which is soluble in tetrahydrofuran THF, were measured by gel permeation chromatography (Chapter 2).

Fig. 3.23 shows the dependence of the number-average molecular weight $\bar{M}n$ on processing time in both the absence and presence of DBTM and lubricant mixture consisting of 0.65% Wax E and 0.8% CaSt. It is observed that the changes in $\bar{M}n$ are not very appreciable, indicating that both cross-linking and chain scission reactions are intimately involved in the mechanochemical degradation of PVC. Consequently, only very little changes occur in the values of $\bar{M}n$. The results obtained in the presence of both DBTM and lubricants are similar to that of the control sample without additives, fig. 3.23 (a,b and c). This result further indicates that neither DBTM nor lubricants preferentially

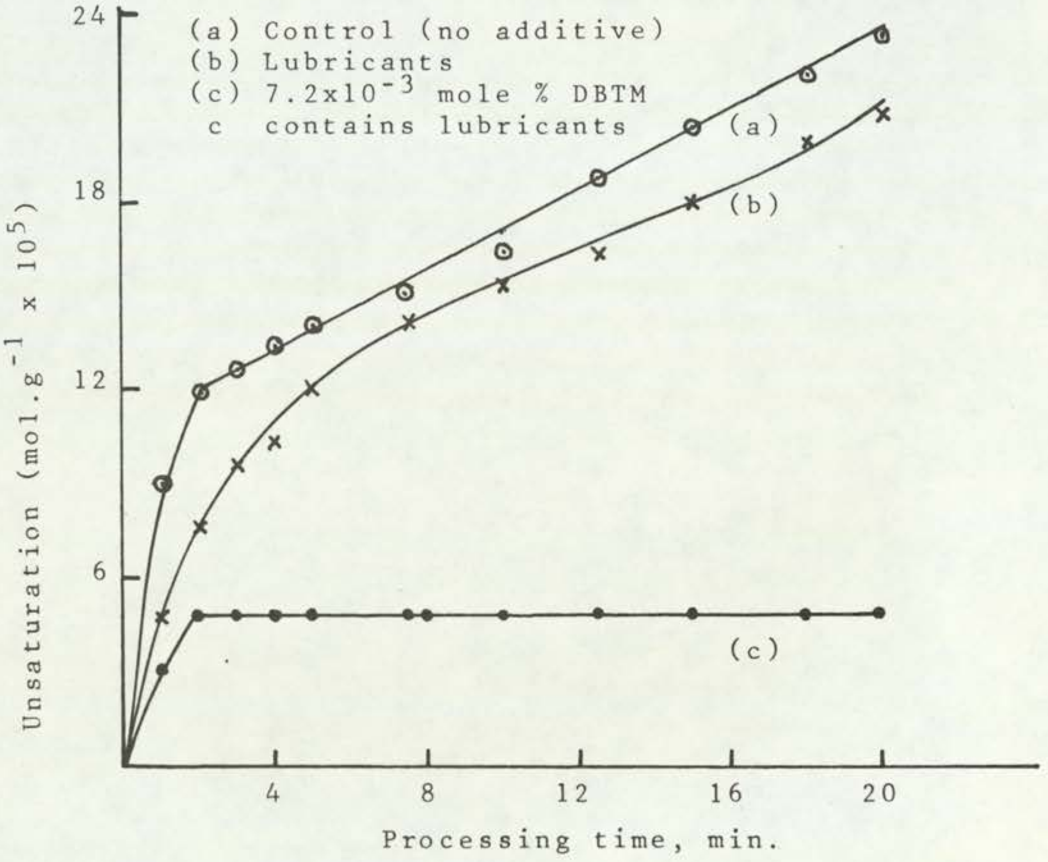


Fig. 3.19: Effect of thermal processing at 180oC on unsaturation in PVC.

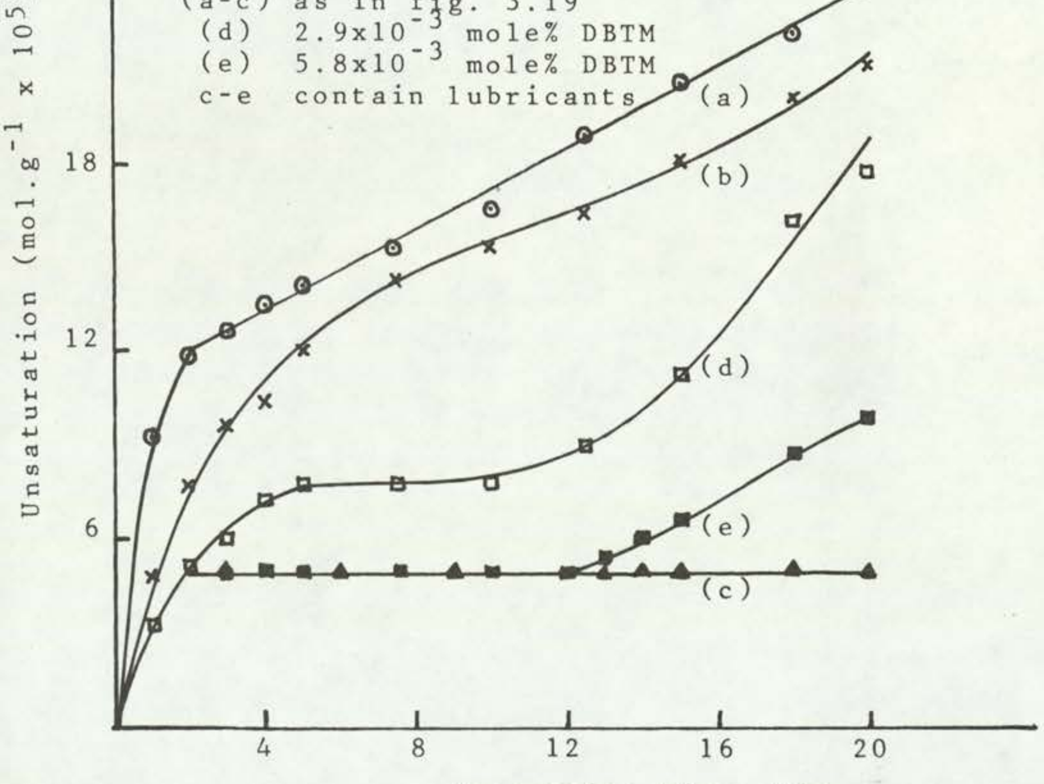


Fig. 3.20: Effect of thermal processing at 180°C on unsaturation in PVC: dependence on DBTM concentration.

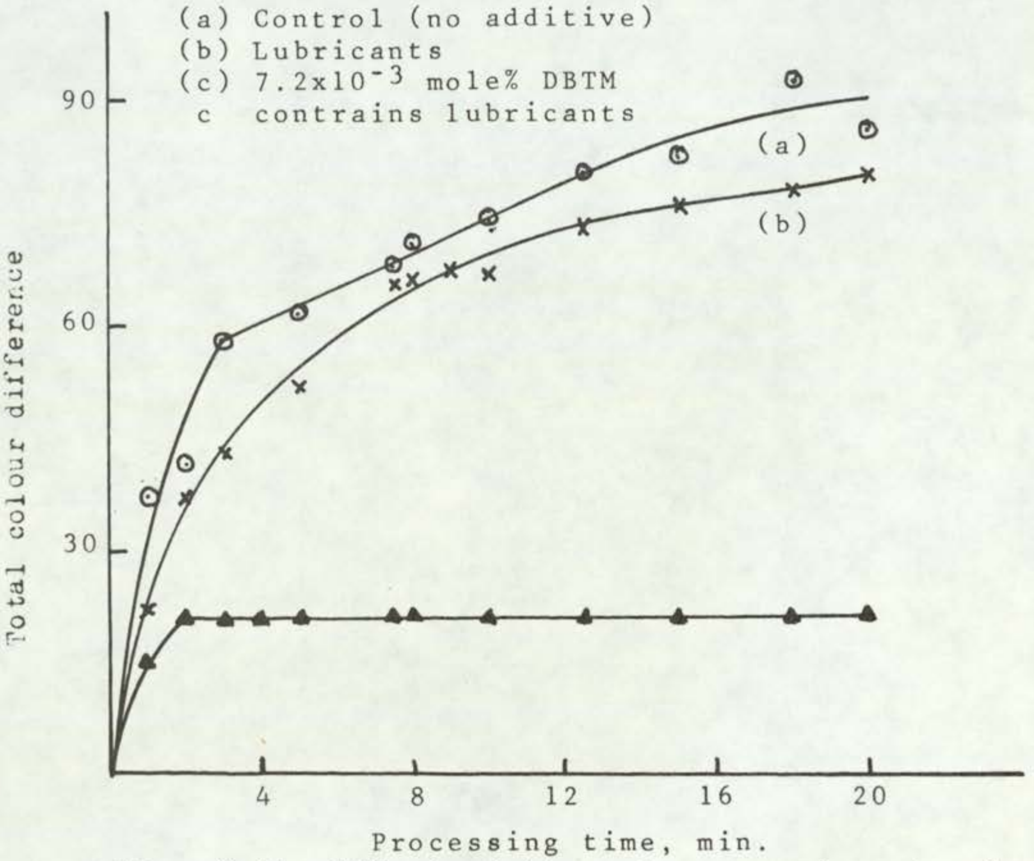


Fig. 3.21: Effect of thermal processing at colour formation in PVC.

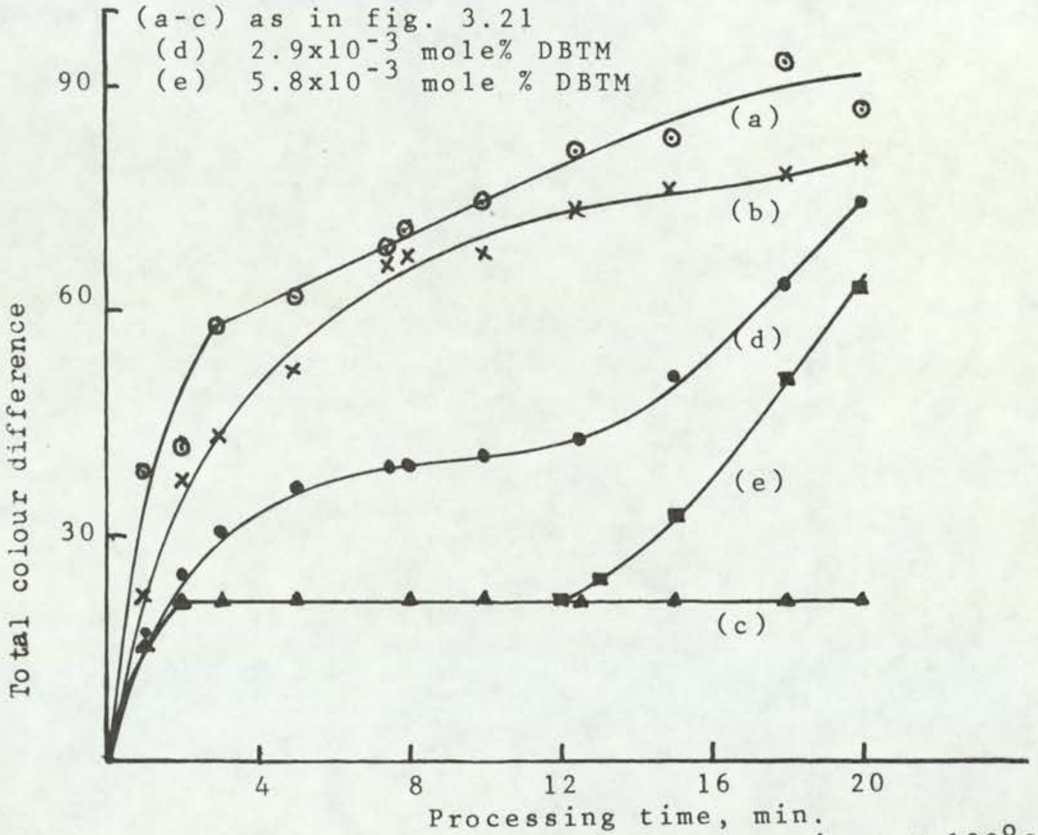


Fig. 3.22: Effect of thermal processing at 180°C on colour formation in PVC: dependence on DBTM concentration.

promotes one of the processes-chain scission and cross-linking-over the other during the processing of the polymer.

The dependence of the other molecular weight averages on processing time are shown in figs. 3.24-28. Unlike $\bar{M}n$, pronounced variations are observed in other molecular weight averages $\bar{M}v$, $\bar{M}w$ and $\bar{M}z$, the derivation of which is discussed below.

The determination of the molecular weight of a polymer sample containing molecules of different sizes i.e. a polydisperse polymer, yields a value called "average molecular weight" as the polymer sample cannot be characterised by a single molecular weight. The nature of the averaging process depends on the property being measured and the magnitude of the average molecular weight tends to increase with increasing sensitivity of the measured effects to the weight of a molecule. Various molecular weight averages are defined according to equation 1. In this expression, Ni is the number of molecules of molecular weight Mi

$$\bar{M}_k = \sum_i N_i M_i^k \Big/ \sum_i N_i M_i^{k-1} \qquad (1)$$

(a) **$\underline{\bar{M}n}$**: When K=1, equation 1 defines the number average molecular weight, Mn, which is the arithmetic mean molecular weight of the sample because $\Sigma N_i M_i$ is the weight of the sample and $\Sigma_i Ni$ is the total number of molecules. For $\bar{M}n$, each molecule, irrespective of size (i.e. either large or small) makes the same contribution to the observed effect in the determination of molecular weight by the colligative properties of solutions. This effect remains unchanged if the total weight is shared equally among the molecules of the system. This effect was observed in fig. 3.23 in which $\bar{M}n$ remains virtually unchanged indicating that only a negligible variation occurs in the total number of polymer molecules during the processing of PVC.

(b) **$\bar{M}w$:** When K=2, equation 1 defines the weight-average molecular weight, $\bar{M}w$, so designated because Mi is now multiplied by the weight of molecules in that size class. For $\bar{M}w$, the measured effect is proportional to the molecular weight of the solute, i.e. weight of each molecule present. In this case, the large species are weighed more heavily than in the $\bar{M}n$, so that for any polydisperse sample $\bar{M}w > \bar{M}i$. The two equations for K=1 and K=2 may be represented as:

$$\bar{M}n = \sum_i N_i M_i \Big/ \sum_i N_i = \sum_i N_i M_i \qquad (2)$$

$$\bar{M}w = \sum_i N_i M_i^2 \Big/ \sum_i N_i M_i = \sum_i W_i M_i \qquad (3)$$

where ni and wi are the number and weight fraction respectively of molecules of molecular weight Mi.

The effect of thermal processing on $\bar{M}w$ in the presence and absence of lubricants is shown in fig. 3.24. The unstabilised control sample shows two distinct stages of molecular chain enlargement. The first growth peaks at $7^1/2$ min. after which a slight decrease occurs. A second increase occurs after 13 min giving rise to higher molecular weight species. The lubricant mixture increases the induction period to onset of the first molecular weight increase from 3 to about 6 min.

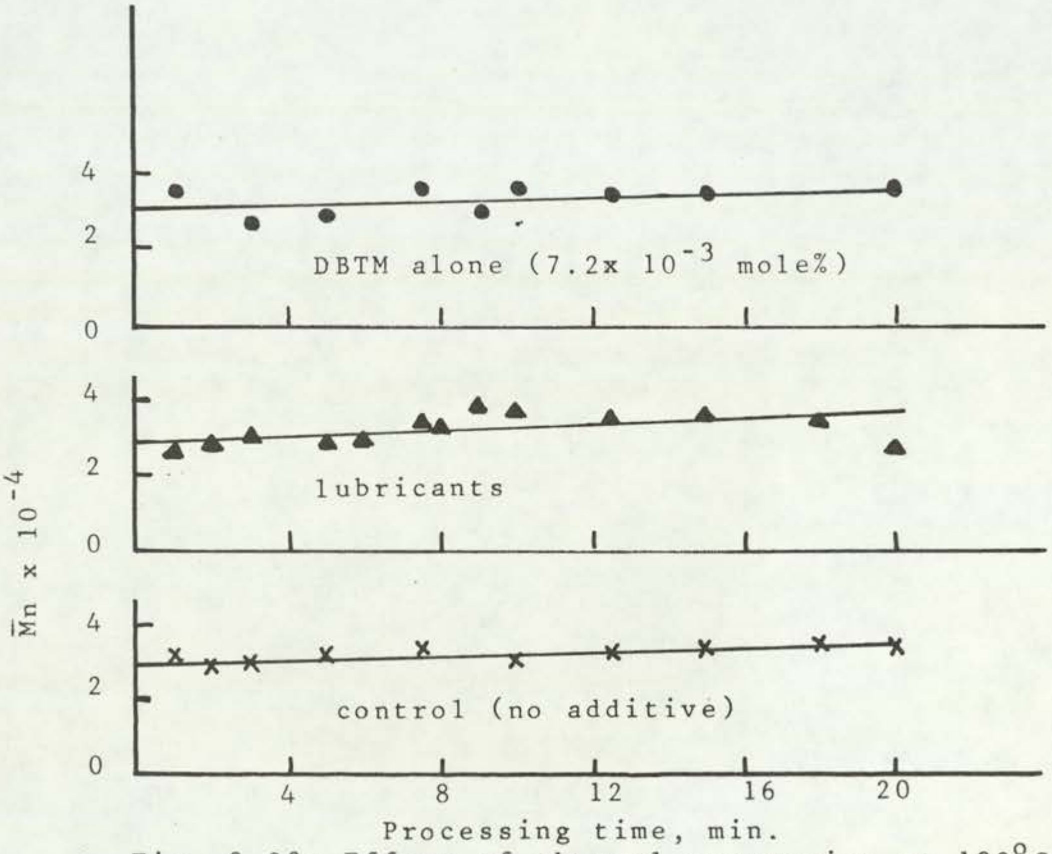


Fig. 3.23: Effect of thermal processing at 180°C on number-average molecular weight of PVC.

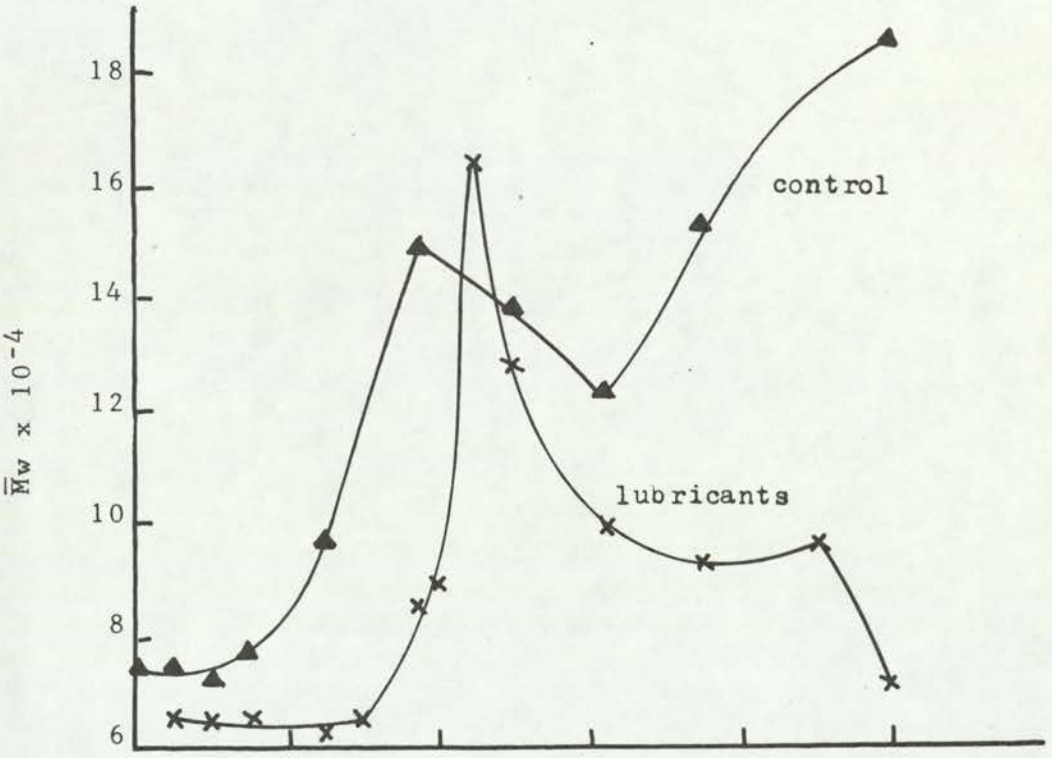


Fig. 3.24: Effect of thermal processing at 180°C on weight-average molecular weight ($\bar{M}w$) of PVC.

and shifts the peak level from $7^1/2$ min. for the control to 9 min. In the presence of lubricants, a large decrease of the first peak is also observed, $\overline{M}w$ falling to lower values than the control sample.

Further, the second molecular weight increase is delayed to a much longer processing time than 20 min.

(c) $\underline{\overline{M}v}$: The viscosity-average molecular weight, $\overline{M}v$ is not an absolute value as other averages and it is formally related to $\overline{M}w$ for linear polymers. Solution viscosity is basically a measure of the size or extension in space of polymer molecules. The simplicity of the measurement and the usefulness of the viscosity-molecular weight correlation are significant and viscosity measurement constitutes an extremely valuable tool for molecular characterisation of polymers. $\overline{M}v$ is defined according to equation 4.

$$\overline{M}v = (\Sigma_i W_i M_i^{a})^{1/a} = (\Sigma_i N_i M_i^{1+a} / \Sigma_i N_i N_i)^{1/a} \qquad (4)$$

where a varies between 0.5 and 1.0 and it is a constant for any specified polymer-solvent pair at any given temperature. $\overline{M}v$ is equal to $\overline{M}w$ when a = 1 and for $a < 1$, $\overline{M}v$ is intermediate in magnitude between $\overline{M}n$ and $\overline{M}w$ but closer to $\overline{M}w$:

The effect of thermal processing on $\overline{M}v$ in the presence and absence of lubricants is shown in fig. 3.25. The features of these curves are similar to those of $\overline{M}w$ in fig. 3.24 and the effect of lubricants again is to increase the induction period to onset of macromolecular enlargement as well as to shift the peak to longer processing time. It is observed however that the peaks of the curves are lower in fig. 3.25 than in fig. 3.24. This observation supports the fact that for any polydisperse polymer sample $\overline{M}v < \overline{M}w$.

(d) **$\overline{M}z$**: When K=3, equation 1 defines the z-average molecular weight, $\overline{M}z$. This is another average which plays a role in the interpretation of the behaviour of polymer solutions. $\overline{M}z$ is influenced by the high molecular weight species even more than $\overline{M}w$. Hence, $\overline{M}z$ depicts the degree of high molecular weight fractions in the polymer sample and may be used as a measure of cross-linking during processing.[127] $\overline{M}z$ may be represented by equation 5.

$$\overline{M}_z = \sum_i N_i M_i^3 / \sum N_i M_i^2 = \sum W_i M_i^2 / \sum W_i M_i \qquad (5)$$

Figure 3.26 shows the effect of thermal processing on $\overline{M}z$ in control sample and in the sample formulated with lubricants. The features of these curves are similar to those obtained for $\overline{M}w$ and $\overline{M}v$ in figs. 3.24 and 25 respectively. However, the peaks of $\overline{M}z$ (fig. 3.26) are significantly higher than those of $\overline{M}w$ and $\overline{M}v$. Also, the decrease in the first peak of fig. 3.26 is more pronounced before the commencement of the second peak in the control sample. The increase and subsequent decrease of $\overline{M}z$ occurs very rapidly in the presence of lubricants, almost all the changes occuring between 8 and 10 min. of procesing.

The changes in all the molecular weight averages during processing in the presence of lubricants and in the presence of 5.8×10^{-3} mole % DBTM are shown in figs. 3.27 and 28 respectively. The correlation

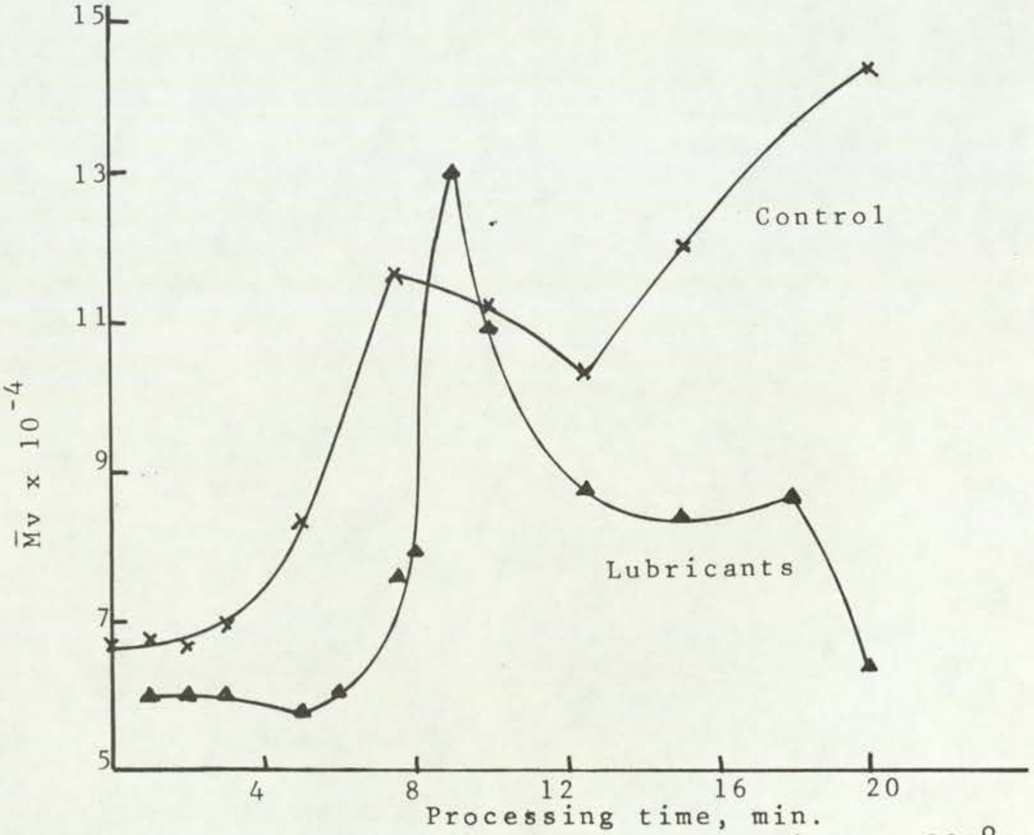


Fig.3.25: Effect of thermal processing at 180°C on viscosity average molecular weight ($\bar{M}v$) of PVC

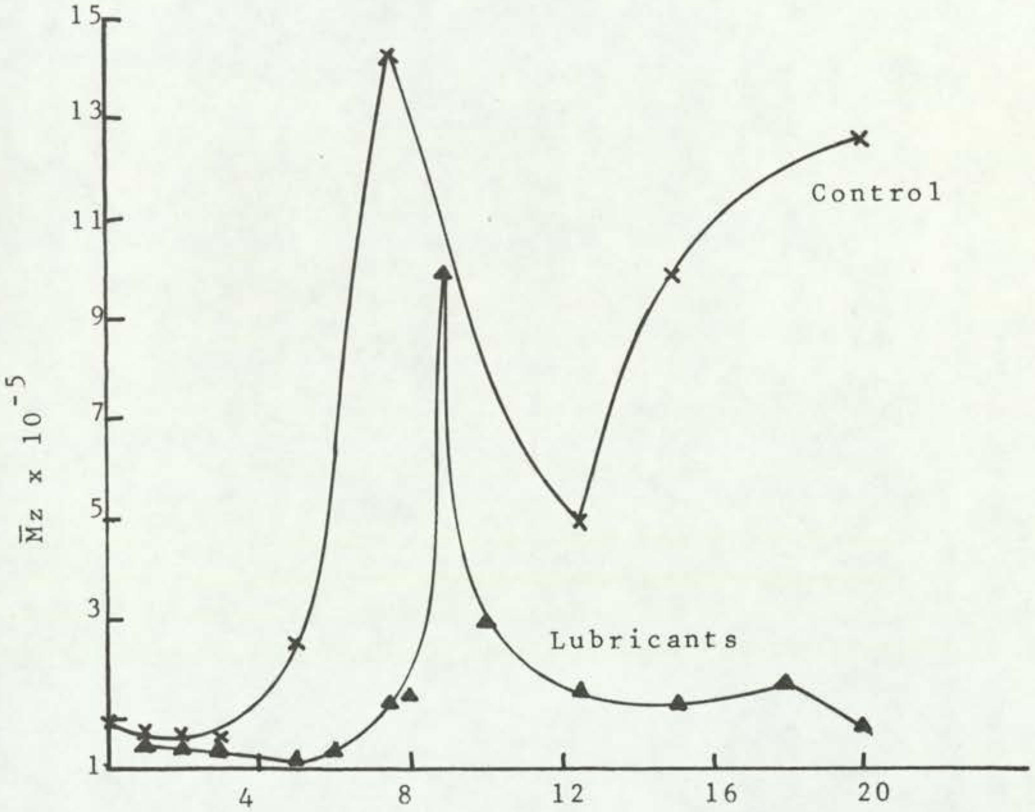


Fig. 3.26: Effect of thermal processing at 180°C on z-average molecular weight ($\bar{M}z$) of PVC.

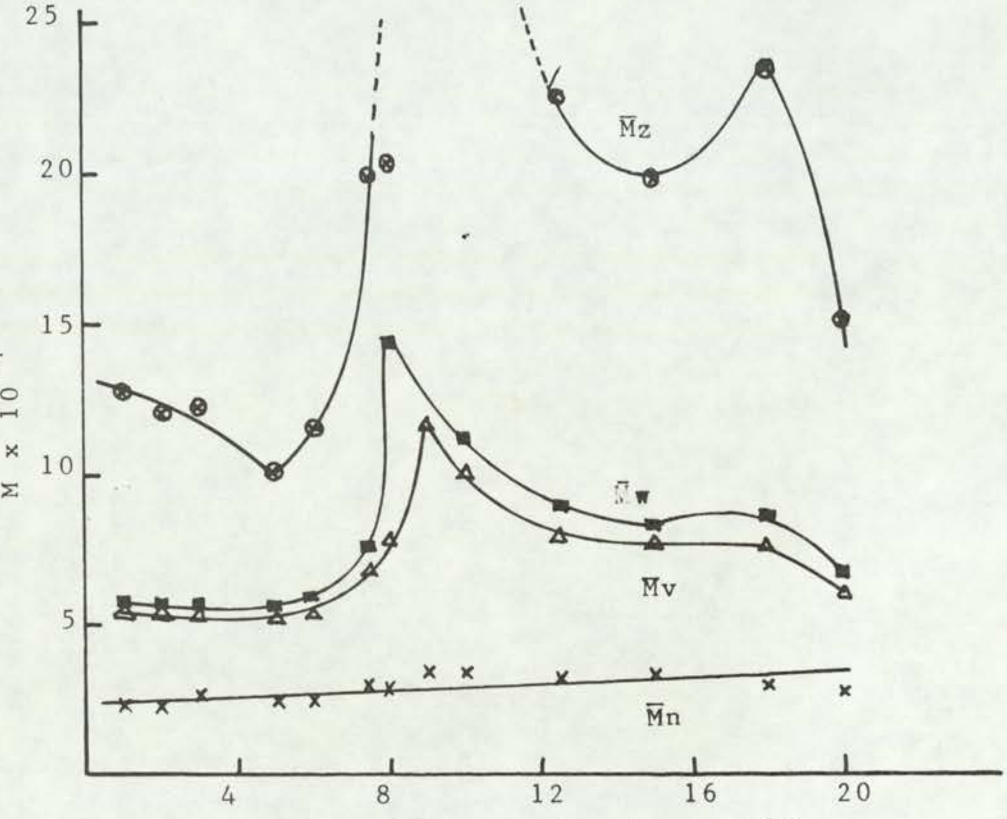


Fig. 3.27: Effect of thermal processing at 180°C on average molecular weights of PVC. Samples contain lubricants.

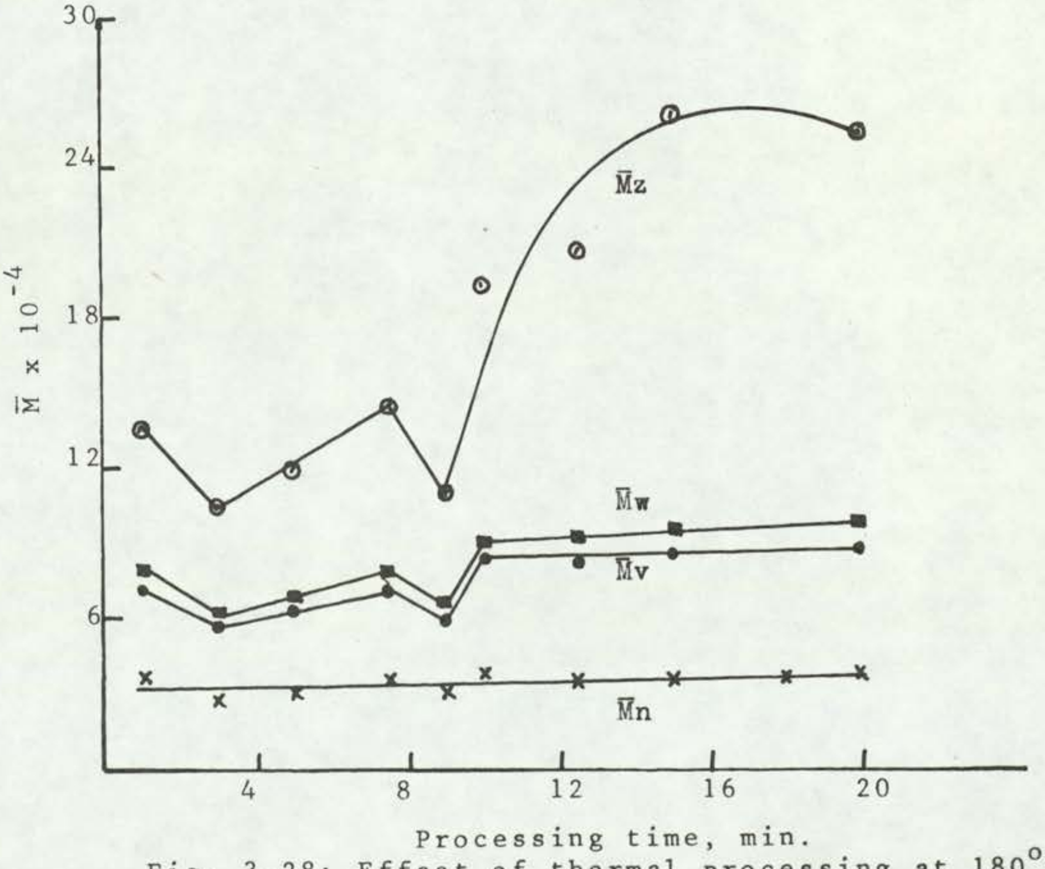


Fig. 3.28: Effect of thermal processing at 180°C on average molecular weights of PVC stabilised with 58×10^{-3} mole% DBTM.

between $\bar{M}v$, $\bar{M}w$ and $\bar{M}z$ is quite striking particularly in the formulations containing lubricants (fig. 3.27). A comparison of the effects of lubricatns with DBTM appears rather difficult on the basis of figs. 3.27 and 28 as an inversion occurs between 8 and 10 min. in samples stabilised with DBTM whereas a peak is observed in the same region in samples containing lubricants. Furthermore, the absolute changes in the values of $\bar{M}v$, $\bar{M}w$ and $\bar{M}z$ are much smaller in the presence of DBTM than lubricants. However, in both cases, the curves of $\bar{M}z$ amplify the changes which occur in the polymer during processing as monitored by both $\bar{M}v$ and $\bar{M}w$ and as predicted by equation 1.

Equation 1 still defines other average molecular weights such as (Z+1)-average molecular weight when K=4, and so on. However, $\bar{M}w$ and $\bar{M}n$ are the most frequently encountered of the absolute averages. Higher averages are of interest only occasionally.

The determination of molecular weights is not merely a matter of academic interest. In engineering applications for example, the tensile strength of a polymer has been correlated with $\bar{M}n$ and melt viscosity with $\bar{M}w$.[128] In general, properties of amorphous polymers such as melt viscosity, softening temperature, tensile and impact strengths, and heat resistance are related to the molecular weight of the polymer chain. Tensile and impact properties of polymers increase rapidly as the chain length increases and then level off. Thus, a range of usefulness may be established in which the polymer chain is of sufficient length, i.e. above the threshold value, to provide minimum useful properties. The melt viscosity continues to increase rapidly as the molecular weight increases above the threshold value. Since polymers with very high molecular weights are difficult to fabricate, an appropriate compromise is usually made between maximising physical properties and processability.

The physical properties of a polymer sample are also related to the degree of polydispersity of the polymer. Although a threshold molecular weight is essential for attainment of the unique properties that characterise high polymers, the polydispersity or molecular weight distribution (MWD) of such polymers affect the useful range of applications. The ratio $\bar{M}w/\bar{M}n$, or more appropriately, $\bar{M}w/\bar{M}n-1$, is frequently used as an index of heterogeneity or polydispersity of the MWD of a polymer sample. The value of the latter ratio is zero for a monodisperse or homogenous polymer for which $\bar{M}w=\bar{M}n$, and the value increases with an increase in the breath of the MWD. The narrower the molecular weight range, the closer are the values of $\bar{M}w$ and $\bar{M}n$. If a polymer sample is completely homogenous, then $\bar{M}n=\bar{M}w=\bar{M}z=\bar{M}z+1$. If it is heterogenous, then invariably, $\bar{M}n \leq \bar{M}w \leq \bar{M}z \leq \bar{M}z+1$. A more precise description of the dependence of flow and ultimate properties of a polymer on molecular weight requires a detailed knowledge of the MWD. The effect of thermal processing on MWD of PVC is examined in the next section.

3.2.3 Molecular Weight Distribution

Data on molecular weight distribution (MWD) were obtained from gel permeation chromatography analyses carried out by RAPRA (Chapter 2).

Figure 3.29 shows the changes in MWD of the fraction of the polymer soluble in THF during the early stages (0-5 min) of thermal processing at 180°C of unstabilised sample of PVC. In this plot, x represents the molecular weight (LogM) of the mean of the MWD while y represents the percentage of the fractions of the mean molecular weight. It is seen from fig. 3.29 that the processing operation reduces the percent abundance of the fractions of the mean molecular weight but increases the polydispersity, broadening at the high molecular weight end of the distribution becoming more pronounced than broadening at the low end of MWD. In severely processed samples of 18 and 20 min. there is a substantial decrease in y as well as a small shift of x to lower values (fig. 3.30). Another striking feature of these curves is the large broadening at high molecular weight end of the distribution whereas the accompanying broadening at the low end is not so prominent. The latter finding may be an indication that under constant shear stress, scission of polymer chain continues until a critical (limiting) chain length is reached such that the spread in the molecular weight of resultant ruptured molecules are minimal whereas the combination of different macroalkyl radicals on the other hand, may produce higher molecules of varying sizes. The reductions in the values of x and y as a result of the processing operation are significant effects in terms of the engineering properties of the polymer sample and of its useful range of applications.

The effect of mild processing on MWD in the presence and absence of DBTM and lubricants is shown in fig. 3.31. After 5 min. of processing, an increase in the high molecular weight fractions

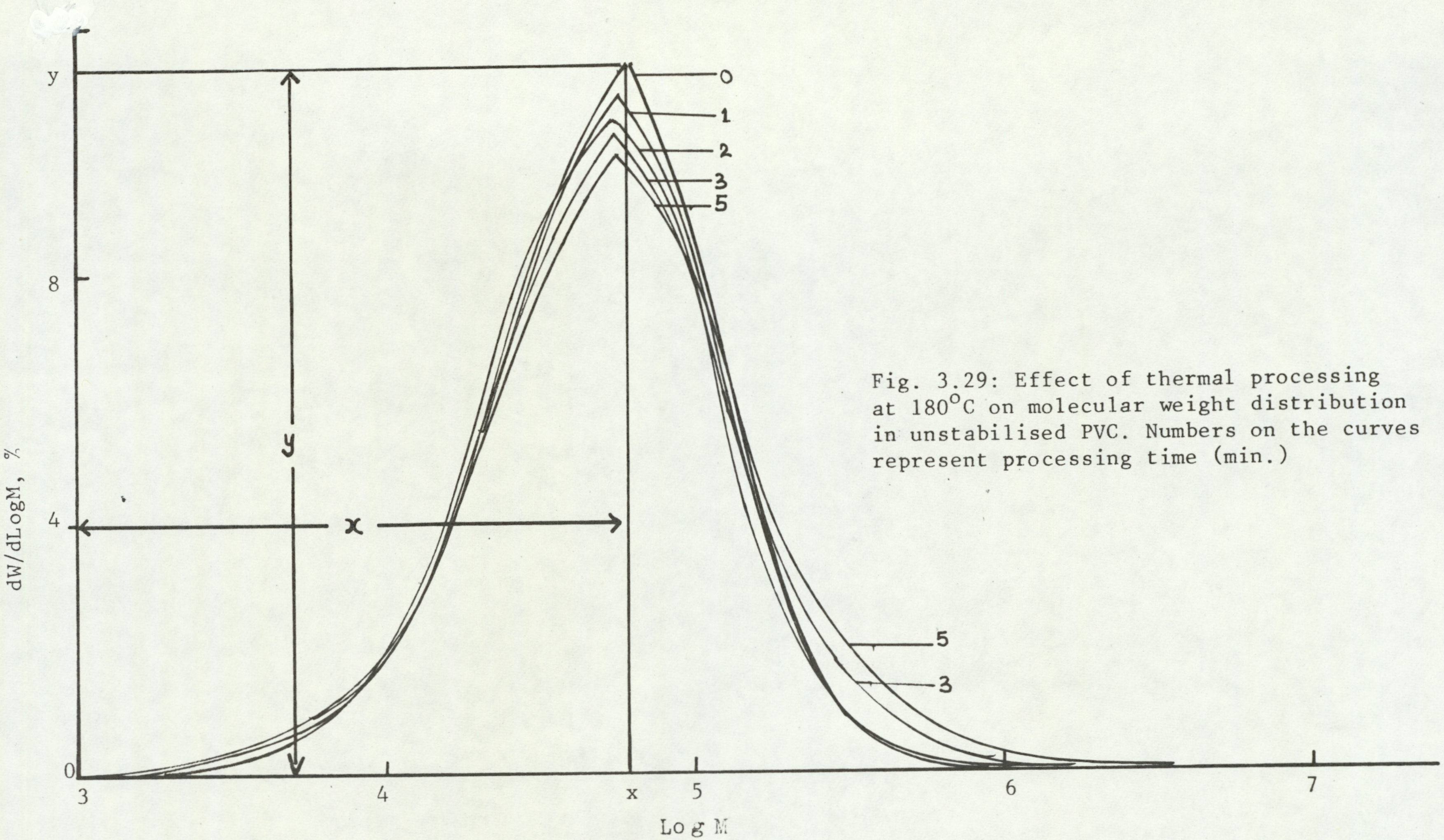


Fig. 3.29: Effect of thermal processing at 180°C on molecular weight distribution in unstabilised PVC. Numbers on the curves represent processing time (min.)

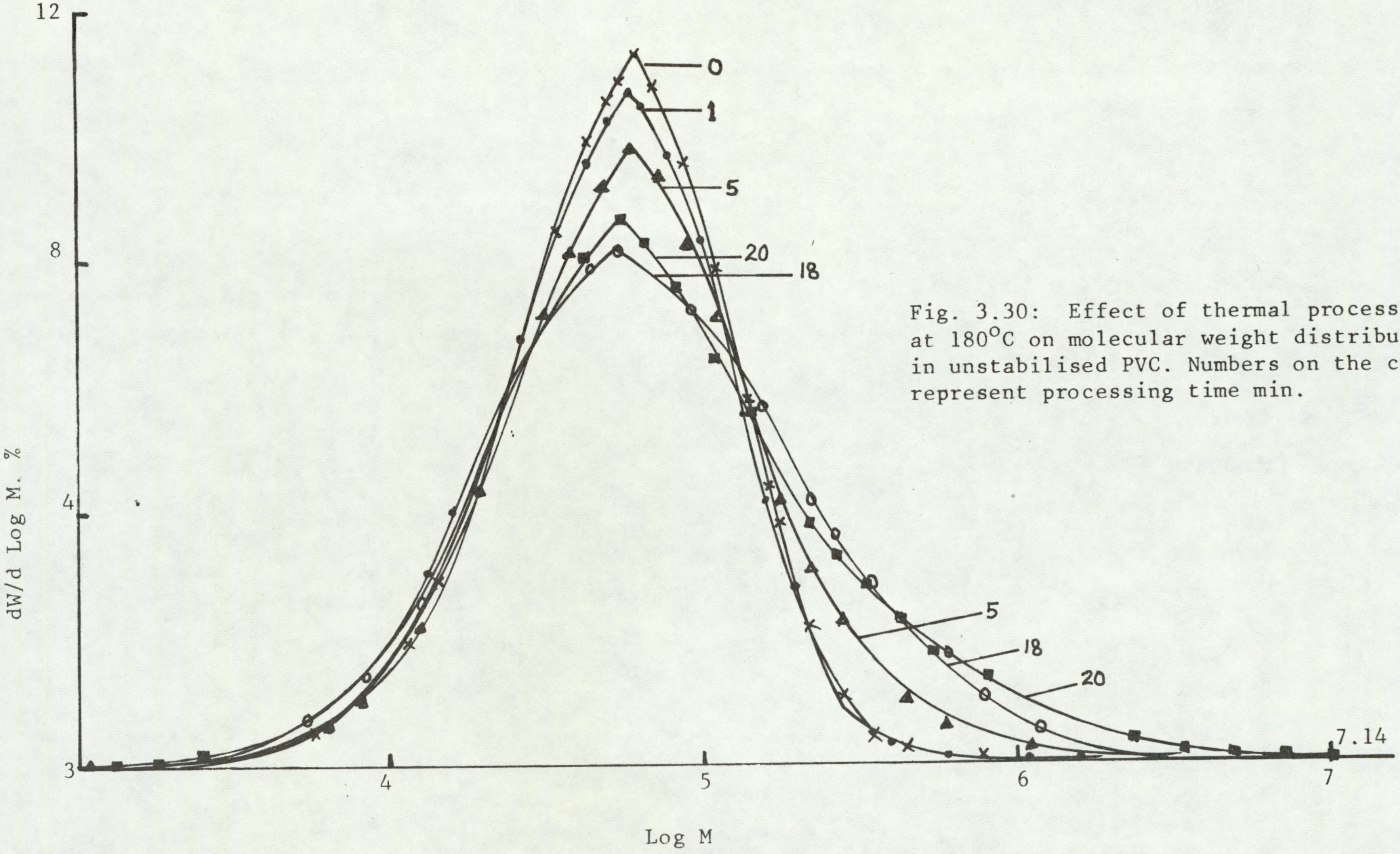


Fig. 3.30: Effect of thermal processing at 180^{o}C on molecular weight distribution in unstabilised PVC. Numbers on the curves represent processing time min.

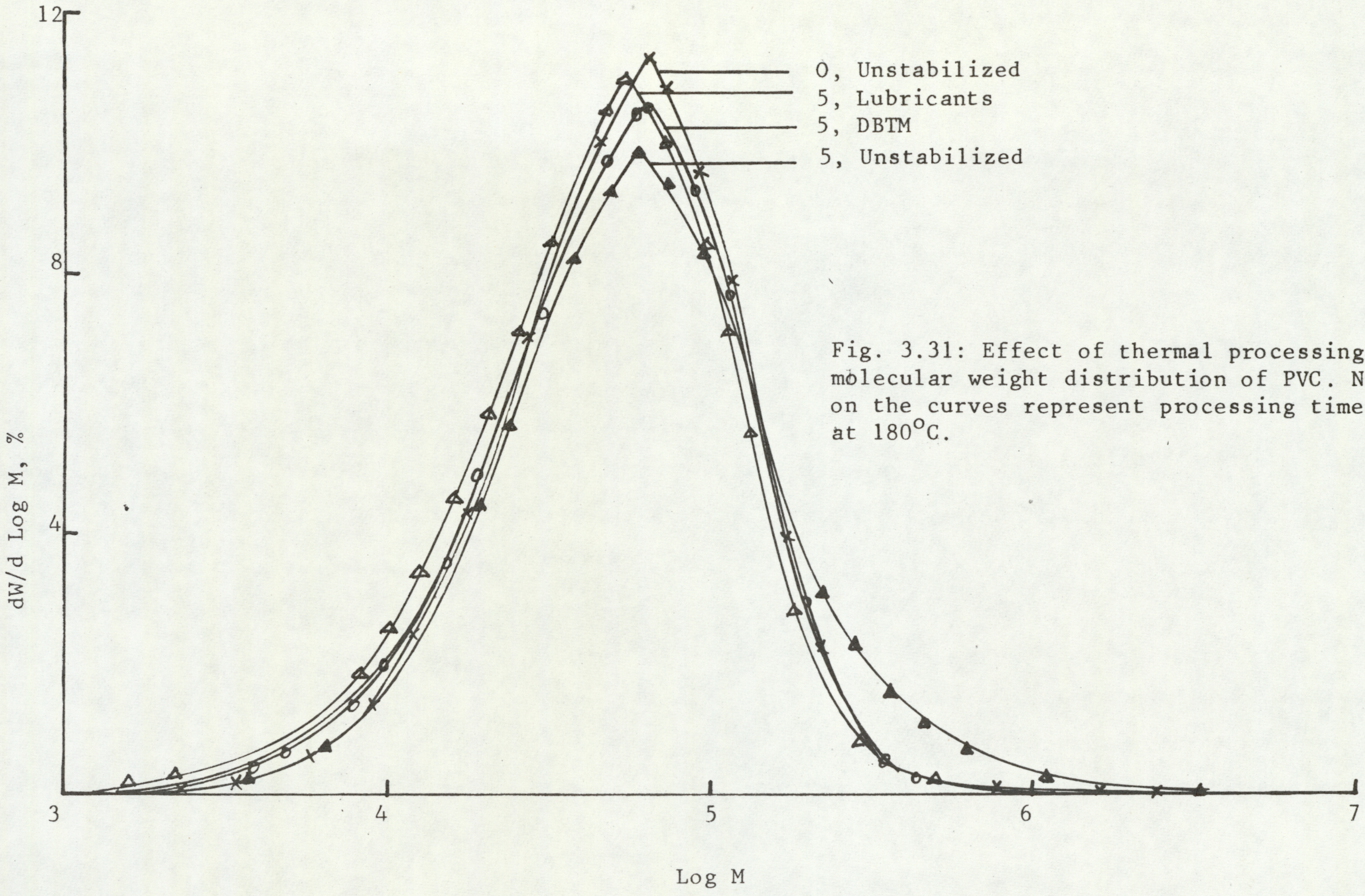


Fig. 3.31: Effect of thermal processing on molecular weight distribution of PVC. Numbers on the curves represent processing time (min) at 180°C.

is noticeable in the control sample with virtually no change at the low end. The lubricant formulation on the other hand leads to broadening at the low end of the distribution with no apparent increase at the high end. In the presence of DBTM, a little broadening is noticeable at the low end, the change at the high end being less detectable. In all cases processing causes a reduction in the percentage of the fraction of the mean molecular weight. It is probable therefore that the most abundant molecules are constantly changed during the thermal mechanochemical process provided that their molecular chain length exceeds the critical or limiting value under the operating shearing stress.[129] The effect of increasing the severity of the processing operation from 5 to 18 min. both in the presence and absence of lubricants is to cause a shift of the MWD to higher weight fractions, the effect being more pronounced in control sample than in formulations containing lubricantts, fig. 3.32. The decrease in the peak fraction, y, is similarly more pronounced for the control sample than for the lubricants. This observation is consistent with the known effect of lubricants in reducing the powerful shearing forces operating on the polymer chains as measured by the torque (see fig. 3.12), which in retrospect limits the "damage" inflicted on the polymer chains as a result of mechanical rupture.

Figure 3.33 shows the changes in MWD after 20 min. of processing both in the presence and absence of Wax E an CaSt which are the components of the synergistic lubricant mixture. The largest decrease in y is observed with Wax E, so also is the increase in high molecular weight species, suggesting that Wax E may have a deleterious effect at long

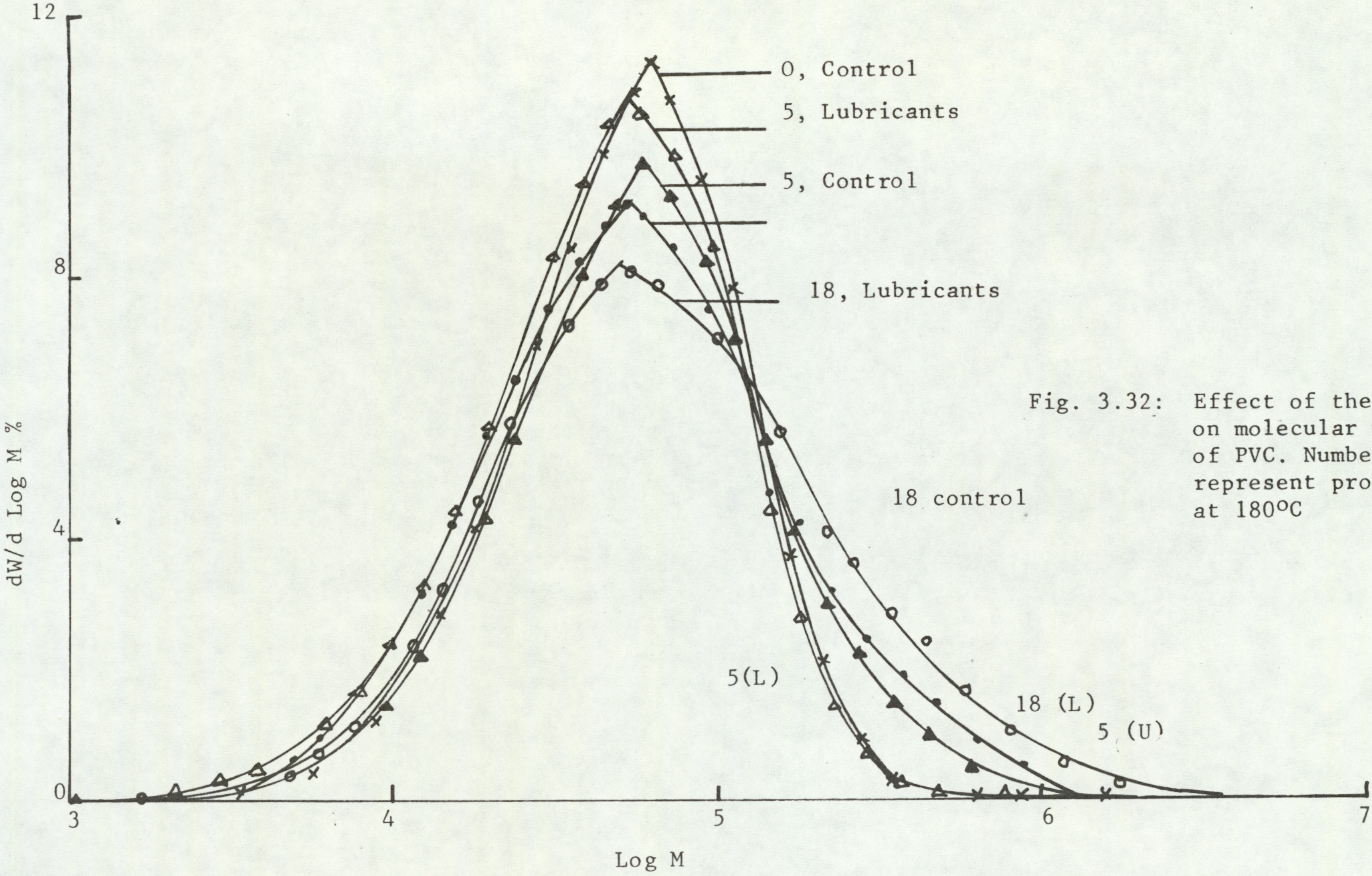


Fig. 3.32: Effect of thermal processing on molecular weight distribution of PVC. Numbers on the curves represent processing time (min) at 180°C

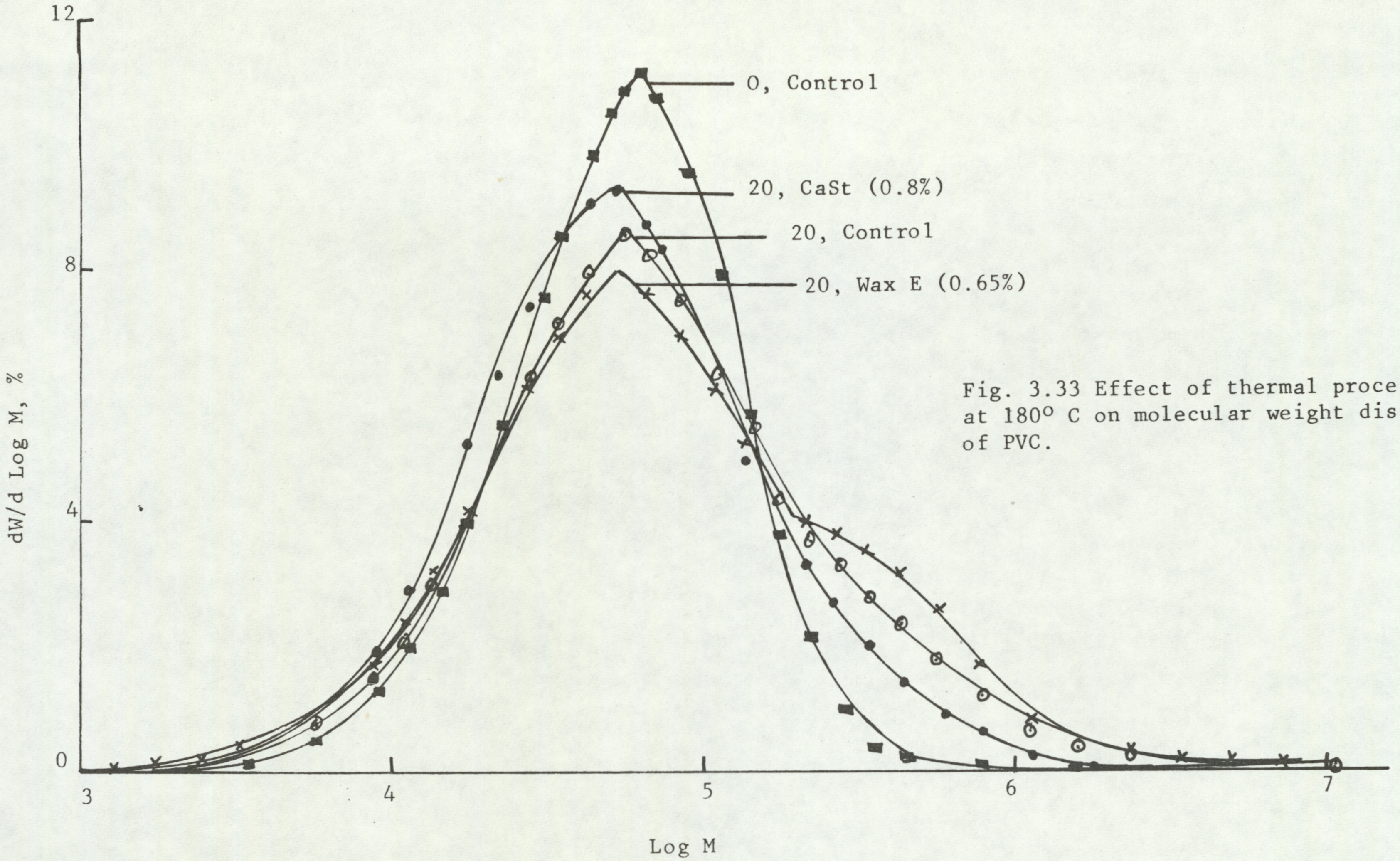


Fig. 3.33 Effect of thermal processing at 180° C on molecular weight distribution of PVC.

processing time. The smallest decrease in y is obtained in the case of CaSt and so also in the broadening at the high molecular weight end of the distribution. The control sample shows an intermediate behaviour between Wax E and CaSt with respect to the above two parameters.

The results discussed above show that during the early stage of processing, the fraction of molecules with the mean molecular weight is reduced, and both lower and higher molecular weight species are formed. Further severe processing leads to greater reduction in dW/dLogM and increased polydispersity with a more pronounced increase of the high molecular weight fractions. The presence of lubricants helps to limit the reduction of dW/dLogM and the polydispersity of the polymer. A similar function is performed by DBTM.

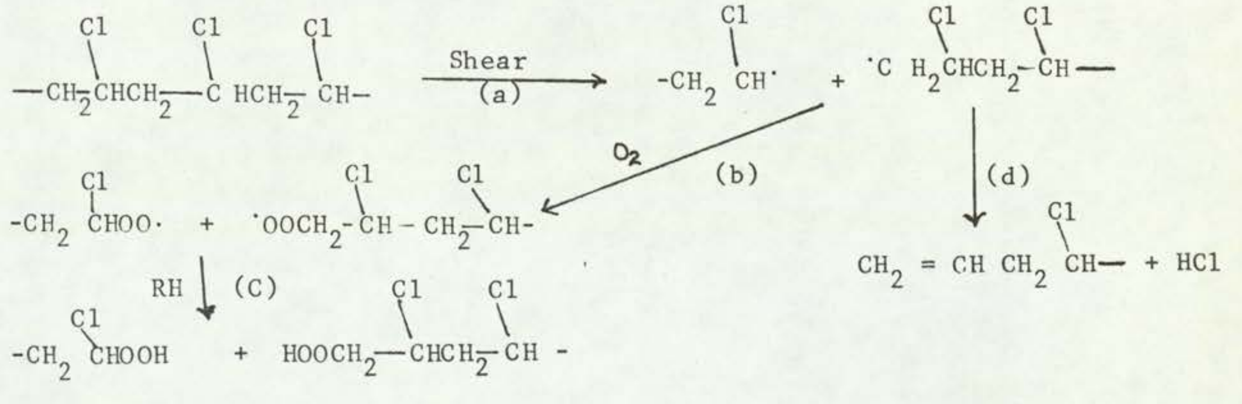
In agreement with the results reported above, Vyvoda[121], Lisitskii and others[130,131] found that the mechanomechanical degradation of PVC is accompanied by chain scission and HCl elimination which led to both molecular weight changes as well as polyene formation and concomitant discolouration. Lubricants were found to lower the rates of the respective reactions by weakening the influence of mechanical stress. Brach adn Bycczkowski,[132] have also reported significant changes in the values of gelation time, temperature during gelation and maximum torque during thermal processing in the presence of lubricating agents. Others[133] reported that the high and low ends of the MWD curves increased after the processing of PVC and it was concluded by Andersson and Sorvik[134] that chain scission occurred only to a very low extent for the low molecular weight samples but was clearly evident for the higher molecular weight samples. This evidence[134] suggests a limiting chain length or weight for the low molecular weight under constant shear and may also explain the greater broadening at the high end than the low end of MWD (see fig. 3.29-33). Ceresa[129] from studies on the effect of mastication of polymers on molecular weight also associated the decrease in the limiting viscosity number of PVC with chain scission as the shear stress causes the polymer molecules to rupture when the shear stress exceeds a critical level. The higher molecular weight species of the polymer were found to rupture at lower critical shear stress, the longer chains being broken before the shorter ones under constant shear stress.

3.3 DISCUSSION

3.3.1 Shear-induced Reactions of PVC

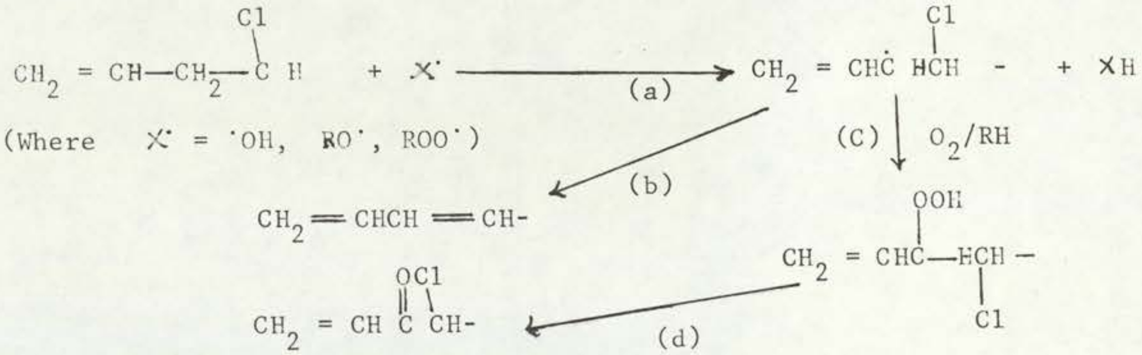
The reactions occuring in PVC during the initial stage of the processing operation involve the scission of the polymer chain by mechanical shear (scheme 3.1)[135] The radicals formed originally can undergo two alternative reactions. They can either react with available oxygen to give alkylperoxyl radicals and ultimately hydroperoxids (scheme 3.1 (b and c)), or they can form the site for dehydrochlorination by loss of a chlorine atom (scheme 3.1 (d)).

Scheme 3.1: Reactions induced by mechanoscission of the PVC chain



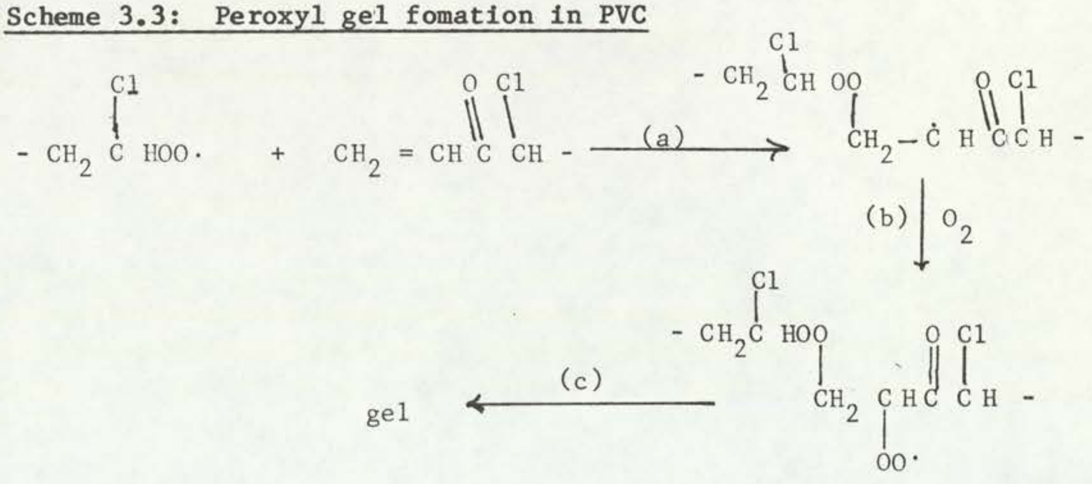
The chlorine atom and the radicals formed from the peroxide species, (i.e. $^{\bullet}OH$, $RO^{\bullet}$ and $ROO^{\bullet}$) may initiate dehydrochlorination, leading to the formation of conjugated unsaturation (scheme 3.2).[53, 54, 77] In the presence of residual oxygen, attack on the allylic radical may also occur leding to the formation of conjugated carbonyl by thermolysis (scheme 3.2 (c and d)).

Scheme 3.2. Reactions of allylic groups in PVC



Vinyl compounds, particularly when conjugated, are well known to react with oxygen giving alternating copolymers. Similar reactions may be responsible for the thermally unstable gel formed in PVC (see fig. 3.3) during processing (Scheme 3.3)[53, 54, 77].

Scheme 3.3: Peroxyl gel fomation in PVC



Other unsaturated species formed in the system (particularly $CH_2=CHCH_2CHCl-$ and $CH_2=CHCH=CH-$) may also undergo similar reactions to form gel.

3.3.2 Mechanism of PVC Stablisation by DBTM

On the basis of the effect of thermal processing on PVC discussed above, it is anticipated that PVC additives which modify the mechanochemical process or which react with the reactive species produced during processing may behave as stabilisers. Infrared spectra examination indicates the mode of action of dibutyl tin maleate, DBTM, in stabilising PVC during processing, and at least three processes are clearly involved for the retardation of the development of conjugation and peroxides.[77]

The first process is the replacement of the labile chlorine in the polymer by the formation of an ester group in the polymer.[27,28] The esterification was monitored during the processing operation by the decrease in the i.r. carboxylate absorption of the stabiliser at 1580 cm^{-1}, fig. 3.34, and the formation of the ester group (fig. 3.35). The ester absorption which was initially at 1725 cm^{-1} shifted progresively during the induction period and with increasing processing time to 1750 cm^{-1} indicating that the double bond of the maleic specie was still present initially.[27,28] At the end of the induction period however, the ester was essentially saturated, showing that it has participated in a second stabilising process by reacting with unsaturation present in the polymer possibly by a Diels-Alder

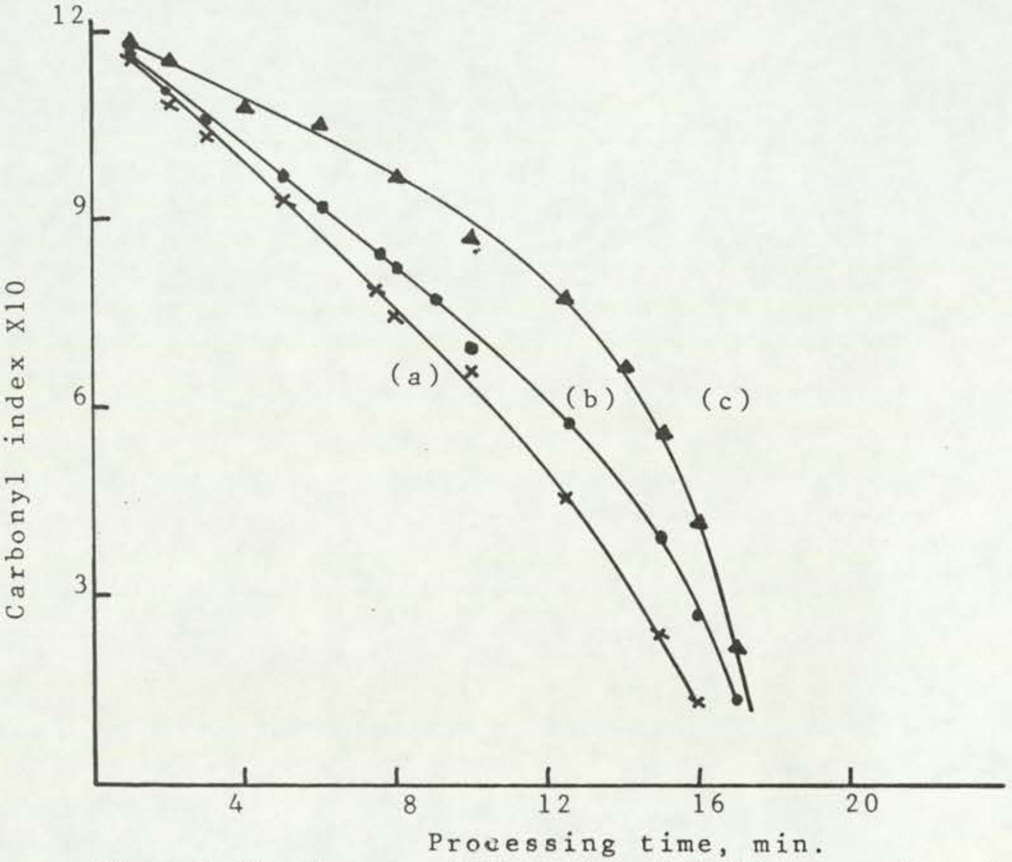


Fig. 3.34: Decay of the tin-stabiliser carboxylate i.r. absorbance at 1580 cm^{-1} in PVC stabilised with 5.8×10^{-3}M DBTM during thermal processing at (a) 170°C, (b) 180°C, (c) 190°C

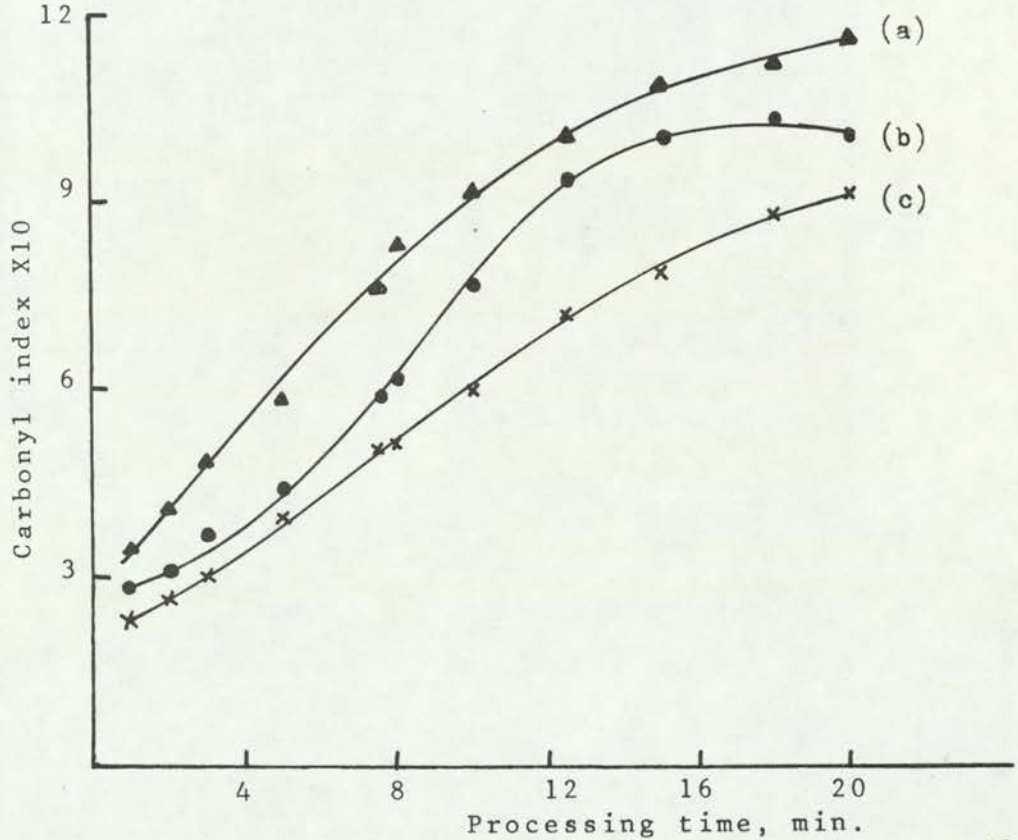


Fig. 3.35: Effect of processing temperature on the maleate ester carbonyl group (i.r. 1720-50 cm^{-1}) in PVC stabilised with 5.8×10^{-3}M DBTM (a) 170°C; (b) 180°C; (c) 190°C.

reaction.[3] In support of this mode of action, lower levels of unsaturation were found in samples stabilised with DBTM than in control samples without additives (see figs. 3.17-22).

Evidence for the third stabilising process was deduced[27] from the formation of free maleic anhydride absorbing at 1775 and 1845 cm^{-1}, the latter being the smaller of the peaks (fig. 3.36). The formation of free maleic anhydride most probably results from the direct attack of HCl on the tin maleate stabiliser. The formation of maleic anhydride was further substantiated by treatment of a sample processed for 10min at 180°C with boiling distilled water for 30 and 60 min and the changes in i.r. spectra were observed (fig. 3.37). The characteristic origianl anhydride carbonyl absorptions at 1775 and 1845 cm^{-1} were substantially reduced and replaced by carbonyl (1715-20cm^{-1}) and carboxylate (1630 and 1605 cm^{-1}) absorptions of the corresponding free acid. An i.r. absorption at 342 cm^{-1} was formed in paralell with the formation of maleic anhydride, indicating the presence of a Sn-Cl bond.[136] Both the maximum formation of ester and of maleic anhydride and the disappearance of the carboxylate occur about the same time, and this time corresponds to the end of the induction period for the formation of conjugated unsaturation and of further peroxides.

The reactions involved in the processes of tin-maleate stabilisation of PVC are shown in scheme 3.4[77].

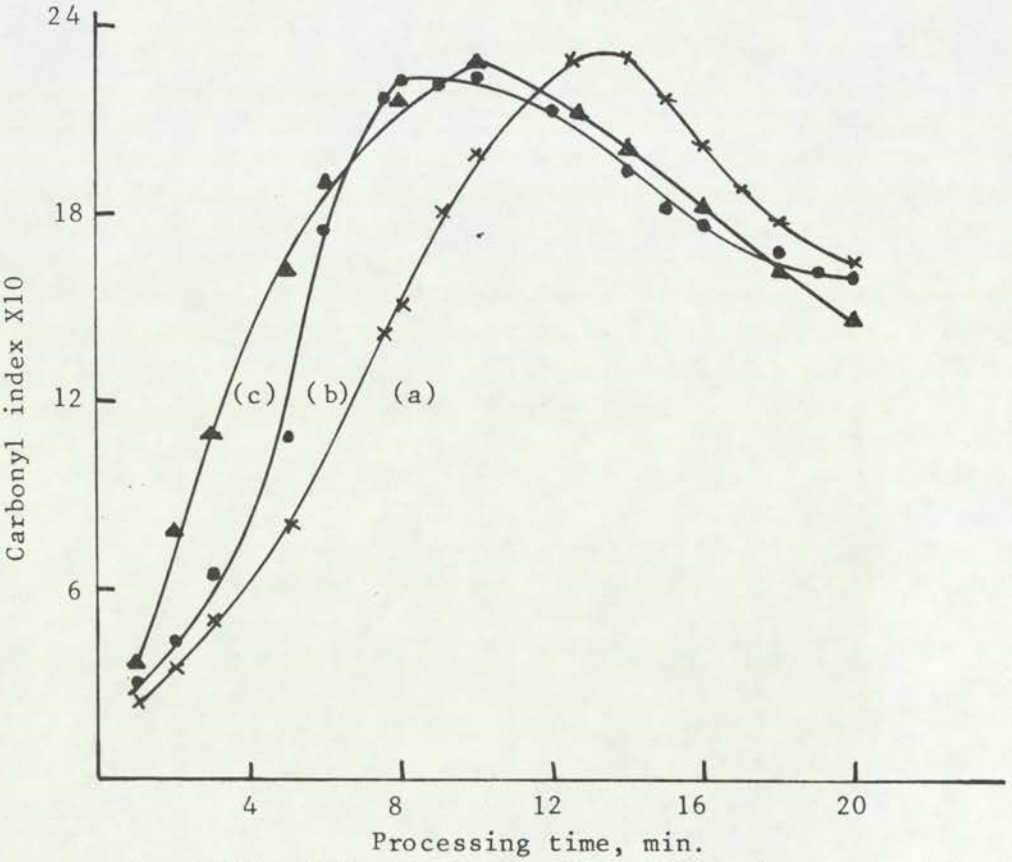


Fig. 3.36: Effect of proeessing temperature on maleic anhydride absorption (i.r. 1780 cm-1) in PVC stabilised with 5.8 x 10^{-3} M DBTM (a) 170oC; (b) 180oC; (c) 190°C.

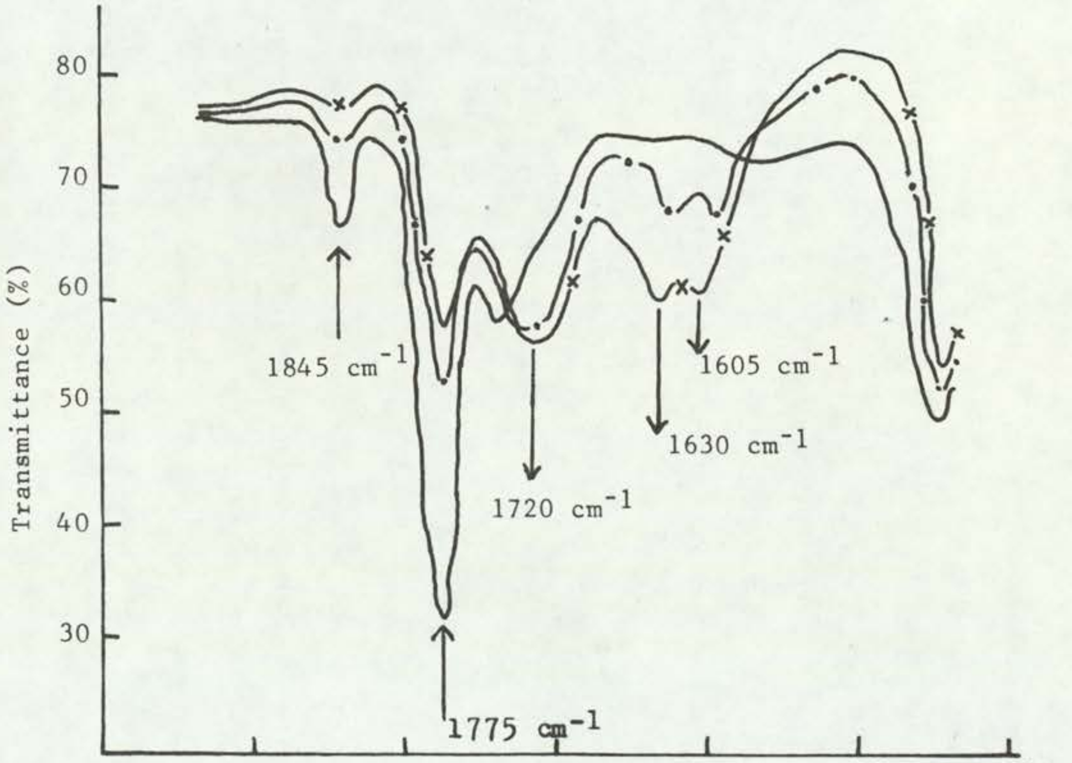
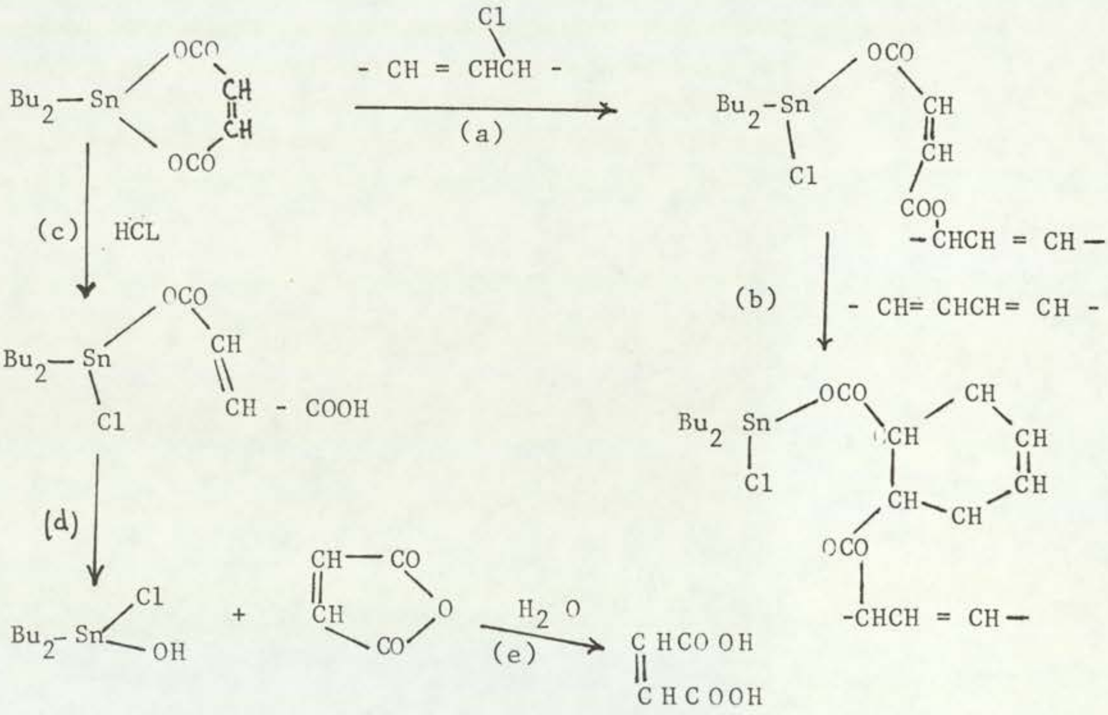
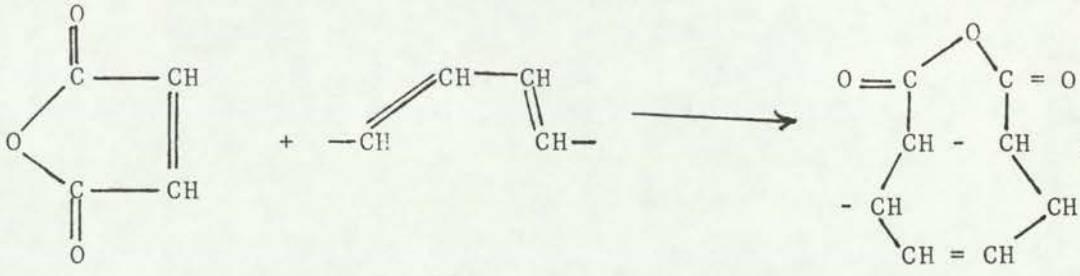


Fig. 3.37: Treatment of processed PVC sample (10 min at 180°C) with boling distilled water. (——)-untreated; (~~-o-~~)- after 30min; (——x——)- after 60 min.

Scheme 3.4: Reactions of tin maleate stabiliser during the thermal induction period of PVC processing



The formation of maleic anhydride as a product of the stabilisation process of PVC by DBTM was confirmed by scheme 3.4 (step e) and this reaction to form the free acid does not from part of the stabilising processes. It is possible however, that maleic anhydride in an alternative reaction may further enhance the "mending" of olefinically degraded polymer chain by a Diels-Alder addition (6)

 (6)

Although a parallel series of reactions occur with CaSt involving esterification of labile chlorine and direct attack of HCl on the metal salt. These processes are much less effective than the tin maleate in retarding the degradation processes occurring in PVC during the processing operation. This is evidenced by the fact that CaSt is much less effective than DBTM in stabilising PVC under the processing conditions. The lubricating effect of CaSt which manifests in the reduction of applied torque (see fig. 3.12) is probably associated with the formation of the free acid which has been shown to possess lubricating properties.[137] The commercial lubricant Wax E, also causes a reduction in polymer chain rupture by reducing the applied torque (see fig. 3.12) and was used in combination with CaSt in PVC formulations.

3.4 Thermal Oxidative Stability of PVC

Films of PVC were subjected to thermal ageing in an air-circulating Wallace oven thermostated at 140°C, and the rates of formation of colour by colourimeter (Colourmaster Model V), unsaturation by chemical methods, and of hydroxyl and carbonyl groups by i.r. spectroscopy were measured.

The effect of processing time on thermal oxidative development of unsaturation is shown in fig. 3.38 for the control sample without additives while the corresponding effect on the total colour difference is shown in fig. 3.39. It is seen that there is a short induction period in the unprocessed sample followed by an autocatalytic formation

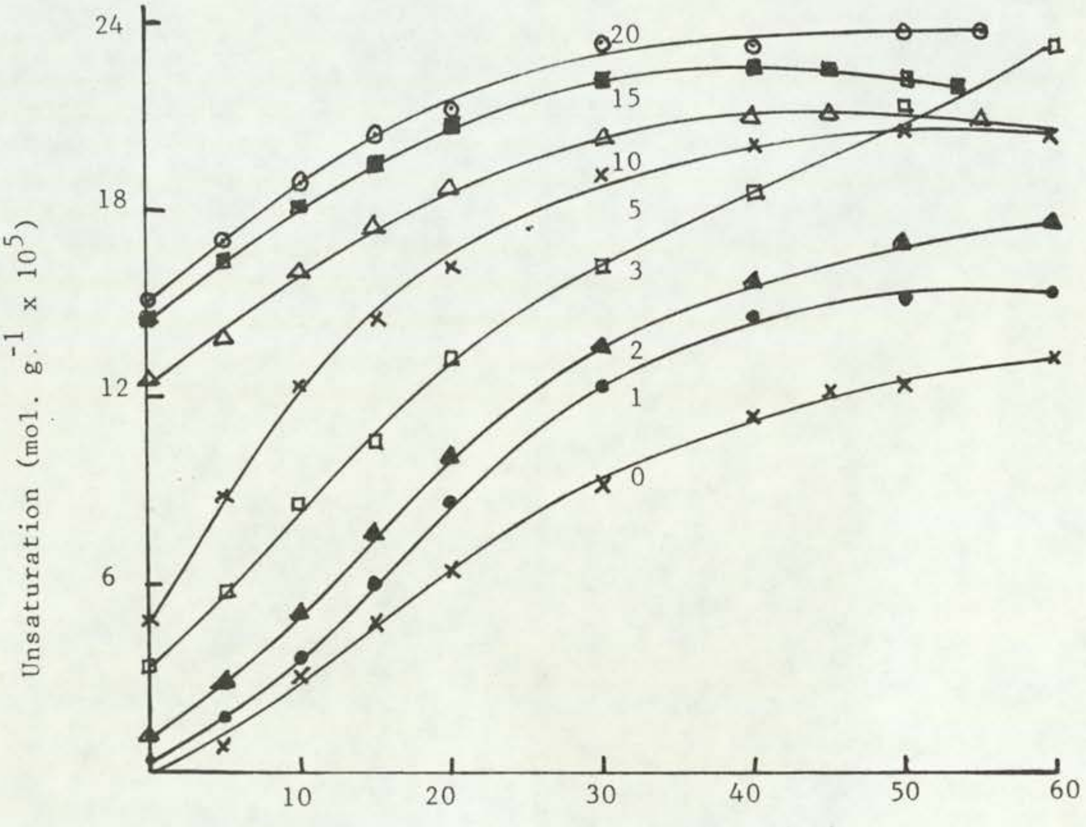


Fig. 3.38: Effect of processing time on the formation of unsaturation in unstabilised PVC. Numbers on the Curves represent processing time (min.) at 180°C.

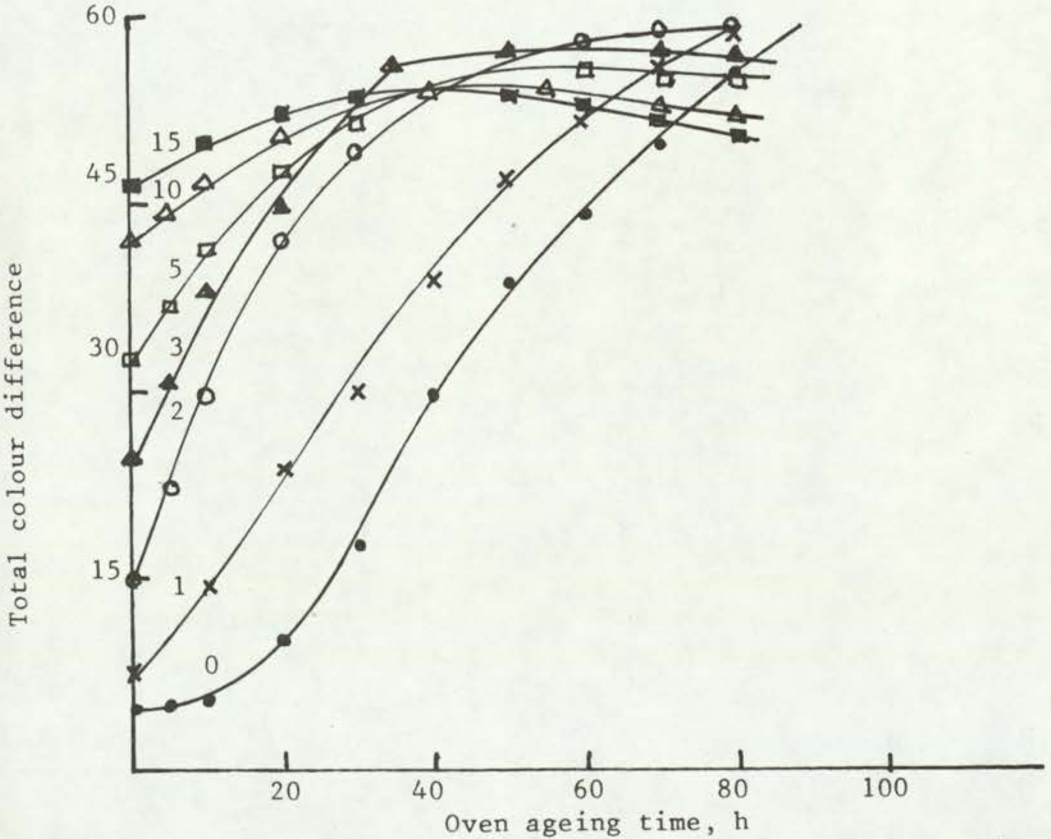


Fig. 3.39: Effect of oven ageing of colour formation in unstabilised PVC. Numbers on the Curves represent processing time (min.) at 180°C.

of both unsaturation and colour. In the processed samples, both unsaturation and colour increase without an initial induction period. The effect of increasing the time of prior processing is to increase the initial concentration of both parameters. The growth in unsaturation during heating at 140°C tends to decrease with increasing time of pre-processing (fig. 3.38). A similar trend may be seen in fig. 3.39 where there is evidence of autoretardation and becoming more pronounced with increasing time of pre-processing. Fig. 3.40 shows the effect of thermal ageing on total colour difference in the presence of lubricants and DBTM for samples pre-processed for 6min. at 180°C. It is seen that the lubricants improve the colour stability of PVC slightly but colour is formed without an induction period. An induction period of about 40h is found in the presence of DBTM followed by a linear formation of colour. A similar result is obtained for the formation of unsaturation in fig. 3.41. The present results agree with the earlier work of Vyvoda[121] and Cooray[138].

Figure 3.42 shows the effect of thermal ageing on carbonyl index. An induction period may be seen in the unprocessed sample whereas for pre-processed samples, growth of carbonyl index commences without any induction period. The induction period in unprocessed sample may probably be due to the time required for the formation of hydroperoxides which may then undergo chemical transformations into carbonyl species, while the former species formed during the processing operation accounts for the immediate formation of carbonyl compounds in pre-processed samples. The formation of hydroxyl index in pre-processed samples during thermal ageing is also compared with the

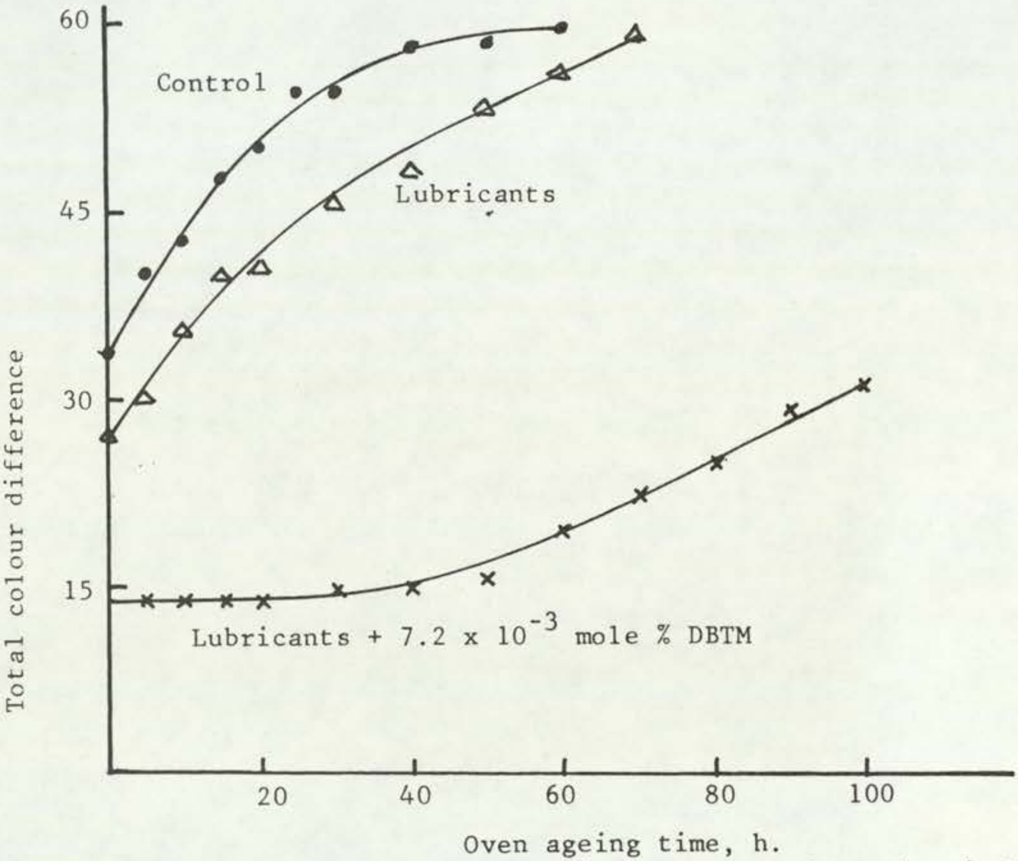


Fig. 3.40: Effect of oven ageing on colour formation in PVC samples processed at 180°C for 6 min.

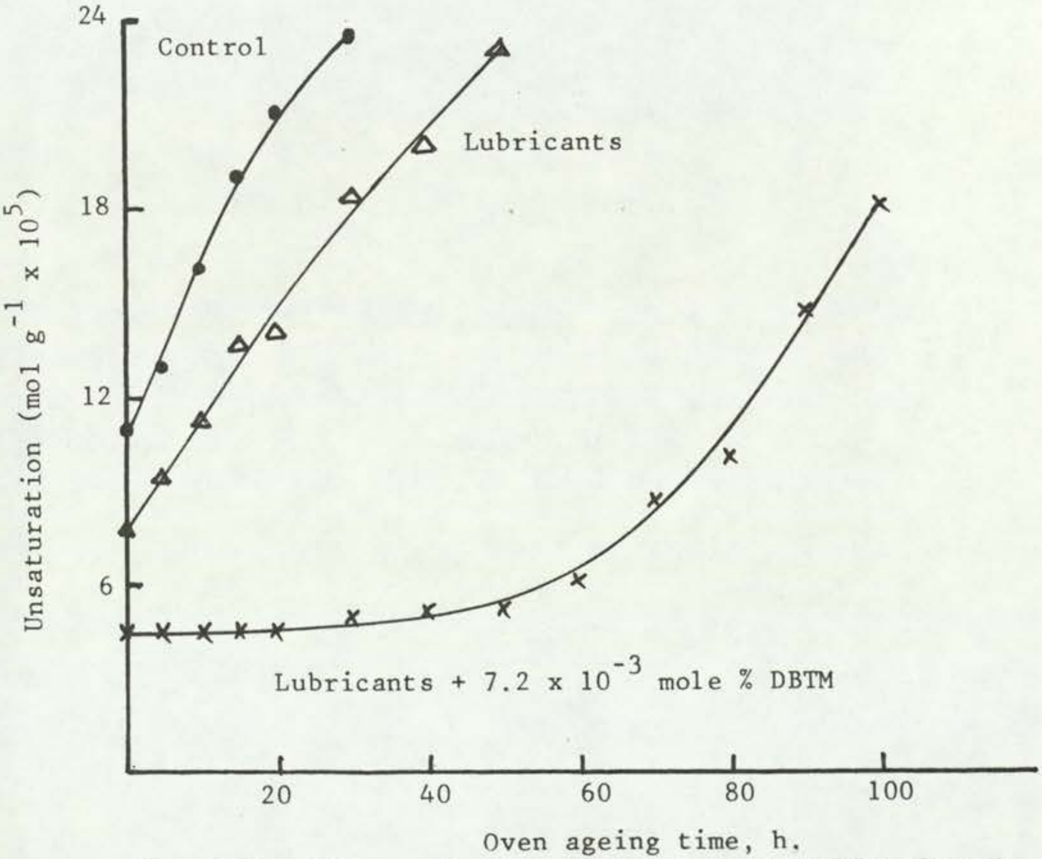


Fig. 3.41: Effect of oven ageing on unsaturation in PVC samples processed at 180°C for 6 min.

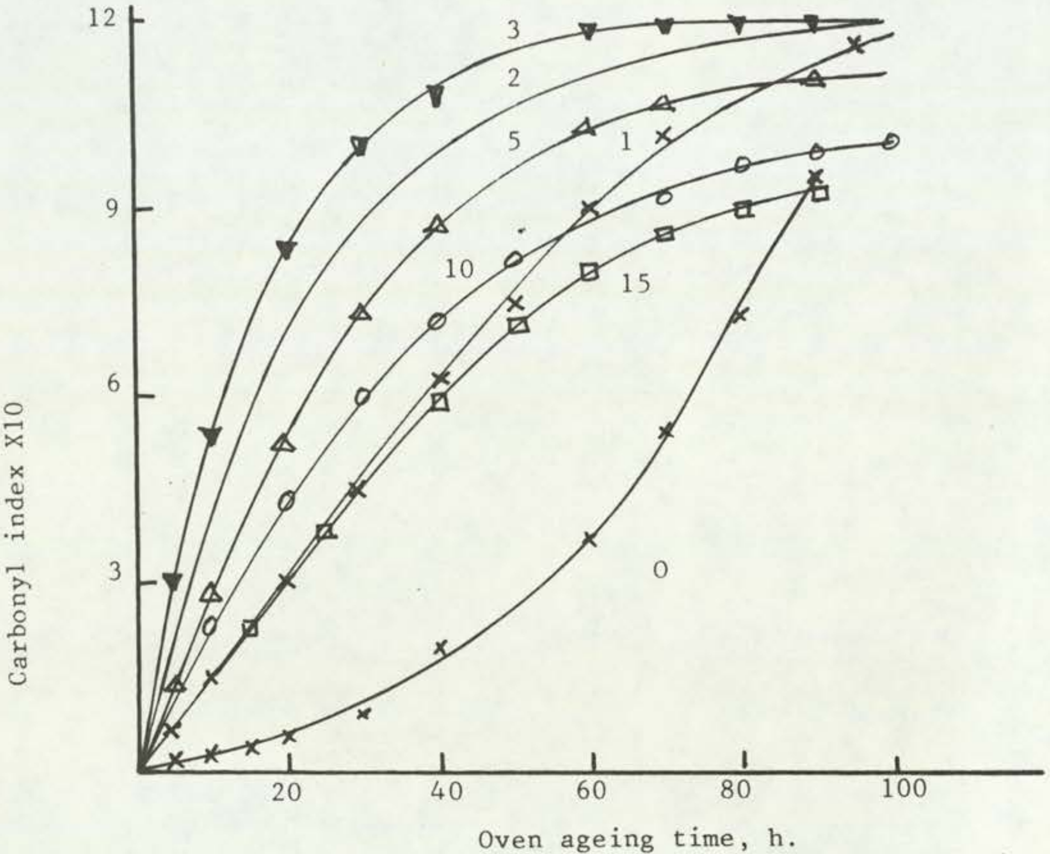


Fig. 3.42: Effect of oven ageing oncarbonyl formation (1715cm^{-1}) in PVC. Numbers on the curves represent processing time (min) at 180°C.

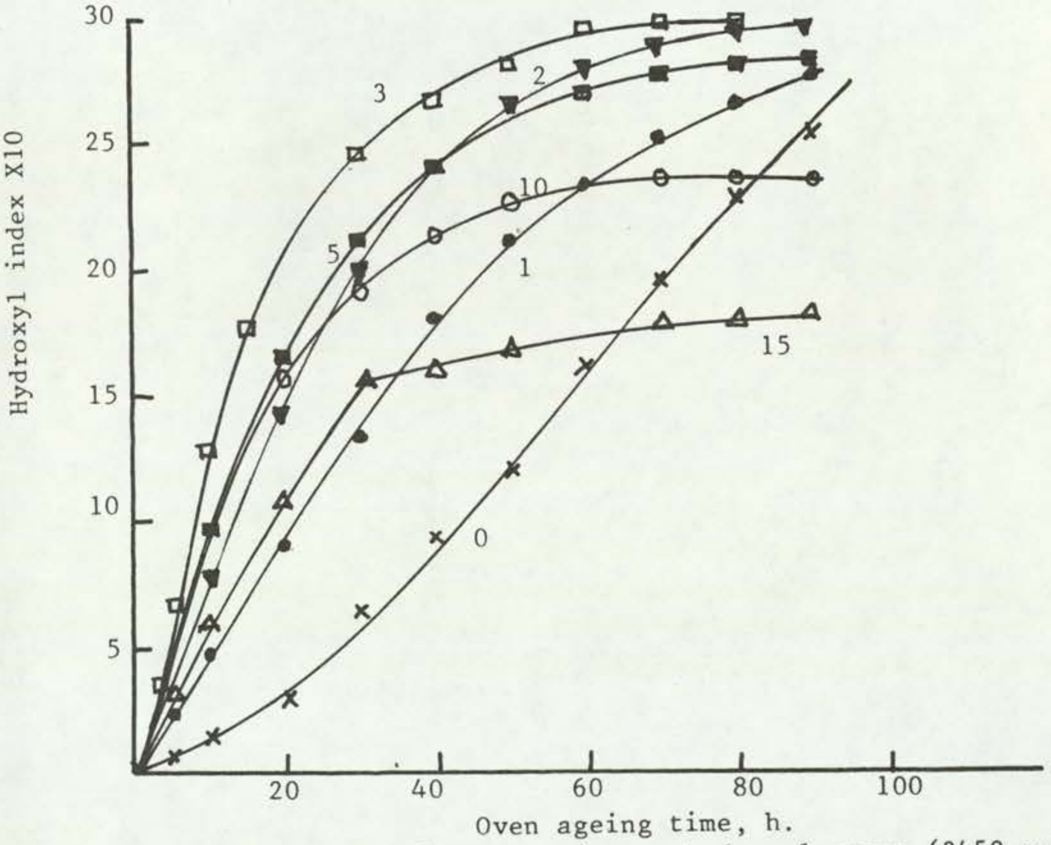


Fig.3.43: Effect of oven ageing on hydroxyl group (3450 cm^{-1}) in PVC. Numbers on curves represent processing time (min) at 180°C.

control, unprocessed sample in figure. 3.43. Again, it may be seen that there is a short induction period to the formation of hydroxyl group in the unprocessed sample whereas the induction period is eliminated in pre-processed samples. However, after an increase from 1 to 3 min, the concentration of hydroxyl index decreases with increasing pre-processing time (5, 10 and 15 min). This decrease in hydroxyl index may suggest further reactions of hydroperoxides in the system.

3.5 Photo - Oxidative Stability of PVC

Samples of PVC were exposed to U.V. irradiation and the rates of formation of unsaturation by chemical method, colour by colourmaster and hydroxyl and carbonyl by i.r spectroscopy were measured.

Figure 3.44 shows the effect of irradiation on the formation of unsaturation in unstabilised PVC. With increasing processing time, there is an increase in initial concentration of unsaturation. The growth of the initial unsaturation tends to decrease with increasing time of pre-processing and autoretardation becomes more pronounced at higher processing time. The effect of irradiation on formation of unsaturation in the presence and absence of lubricants and DBTM is shown in fig. 3.45. It can be seen that lubricants reduce mechanochemically induced formation of unsaturation evidenced by a lower initial unsaturation as well as reducing photo-oxidative development of unsaturation during ultra violet irradiation. The growth of unsaturation in the presence of lubricants is similar to the control sample without additives and occurs without an induction period. DBTM

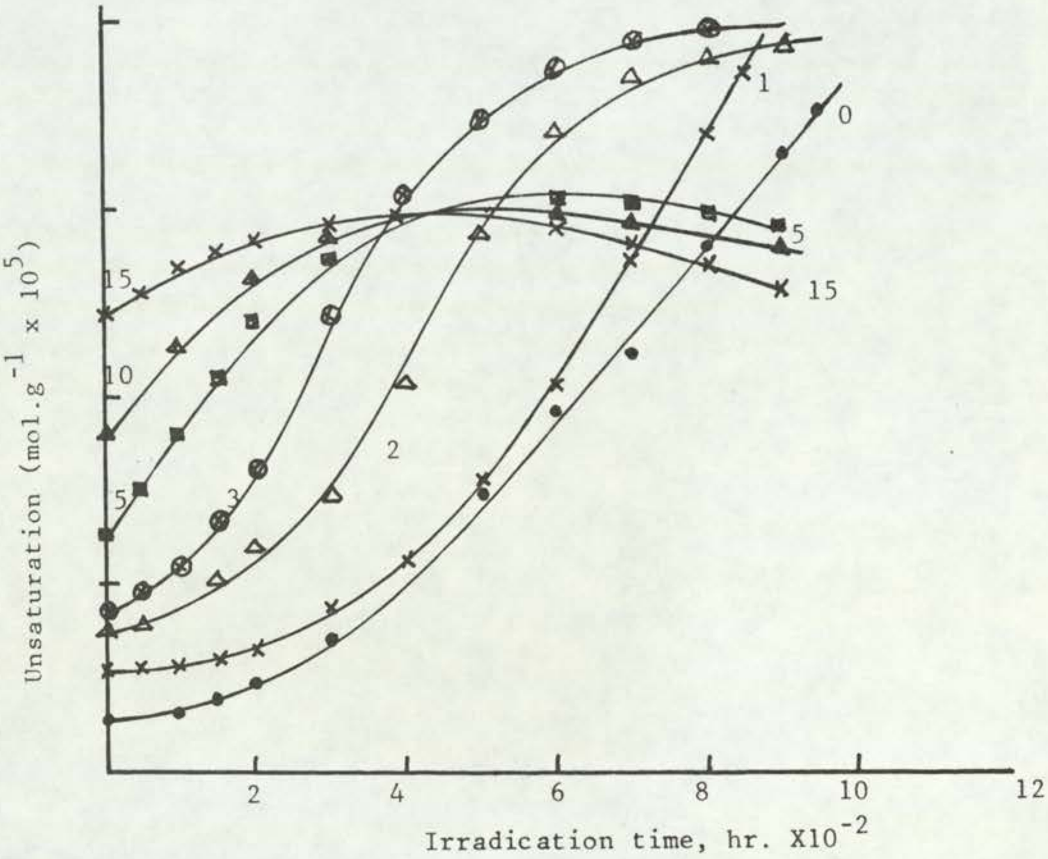


Fig. 3.44: Effect of uv irradiation on unsaturation in PVC
Numbers on the curves represent processing time (min) at 180°C.

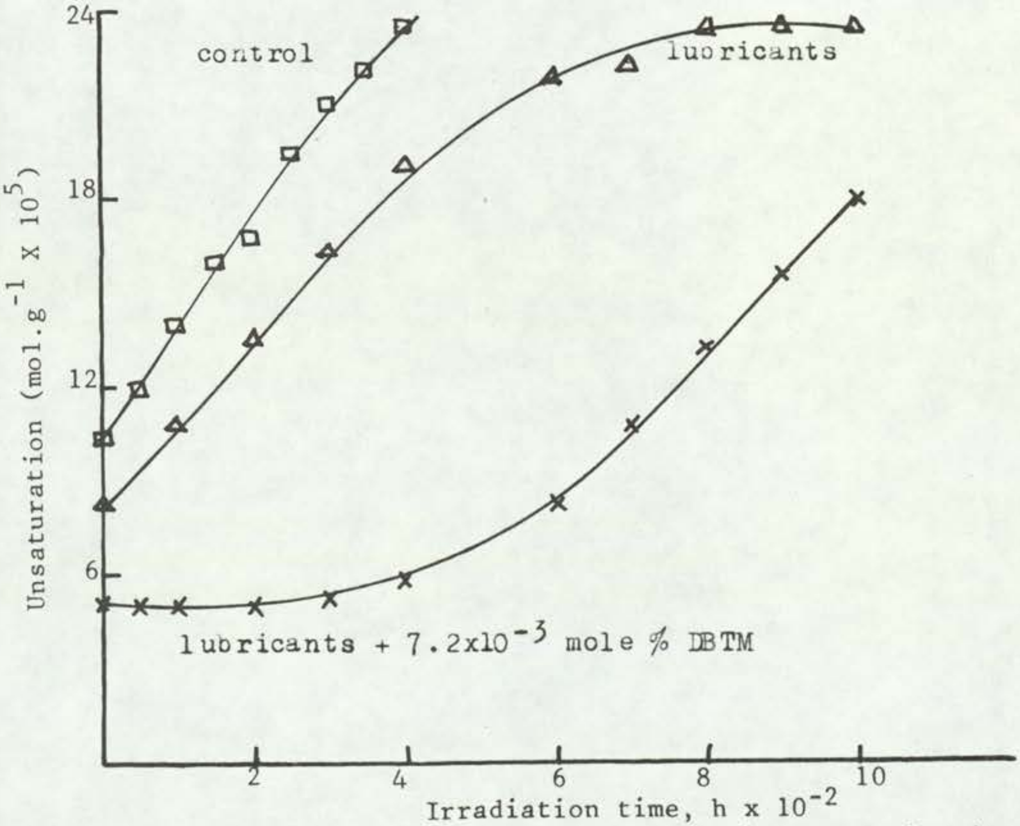


Fig. 3.45 : Effect of uv irradiation on unsaturation in PVC.

causes an induction period to photo-oxidative development of unsaturation after which time a rather linear increase in unsaturation is obtained.

The changes in total colour difference (fig. 3.46) are found to be similar to those of unsaturation (fig. 3.44) An induction period which is absent in pre-processed samples is found in the unprocessed sample and this may suggest that the mechanochemically induced unsaturation introduced into the polymer during the processing operation sensitises the polymer chain to further photo-oxidative formation of unsaturation. Studies in other polymers[139,140] showed that the presence of minor amounts of initial unsaturation is a major cause of subsequent photo-oxidation, as a consequence of allylic hydperoxide formation. It has also been shown[83] that the effect of thermal processing on PVC is to sensitise the polymer to u.v. degradation in the same way and that PVC stabilisers which inhibit the formation of unsaturation or which remove unsaturation by secondary reactions (e.g. dienophiles) also inhibit u.v. degradation. The presence of lubricants helps in reducing total colour formation (fig. 3.47) although the shape of the curve is similar to the control without additives. Incorporation of DBTM gives rise to an induction period of about 300h after which a rapid accumulation of colour occurs.

The rate of photo-oxidation as measured by the carbonyl index during u.v. irradiation of unstabilised PVC pre-processed for different periods at 180°C is shown in fig. 3.48. A rapid accumulation of carbonyl compounds can be seen to occur in the first 3 min. of

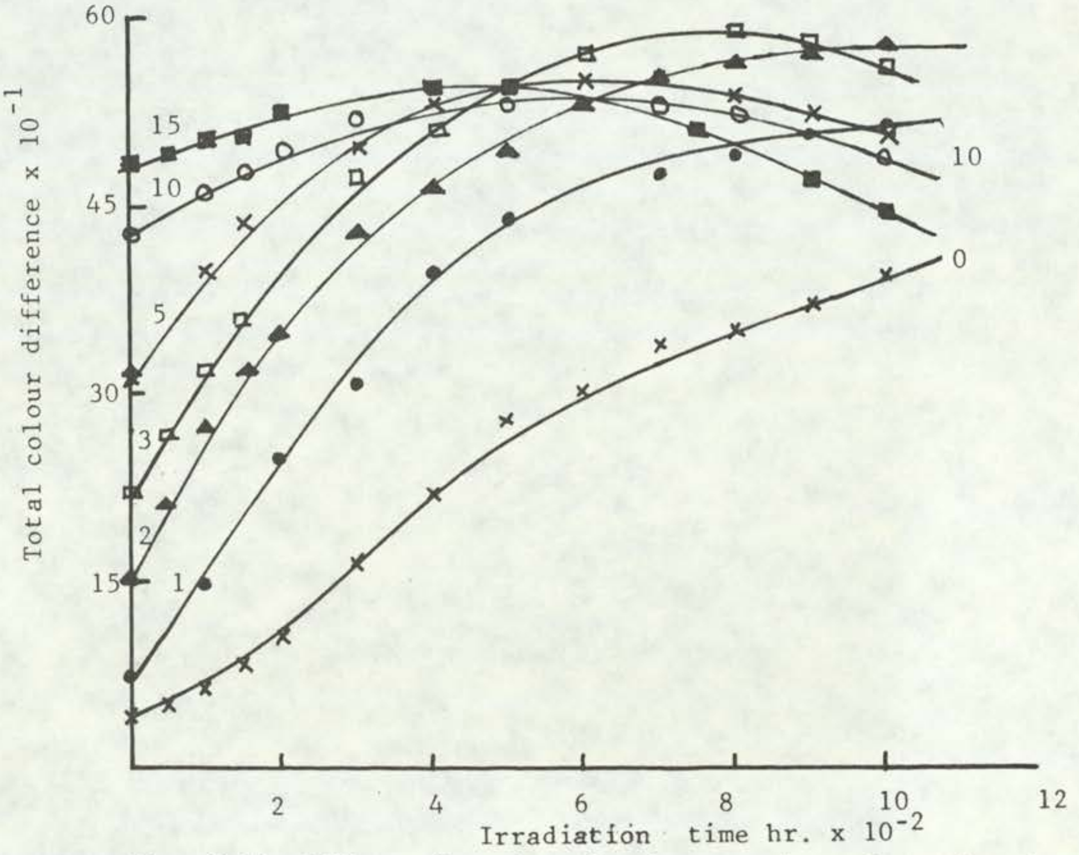


Fig. 3.46: Effect of uv irradiation on colour formation in unstabilised PVC. Numbers on the curves represent processing time (min) at 180°C.

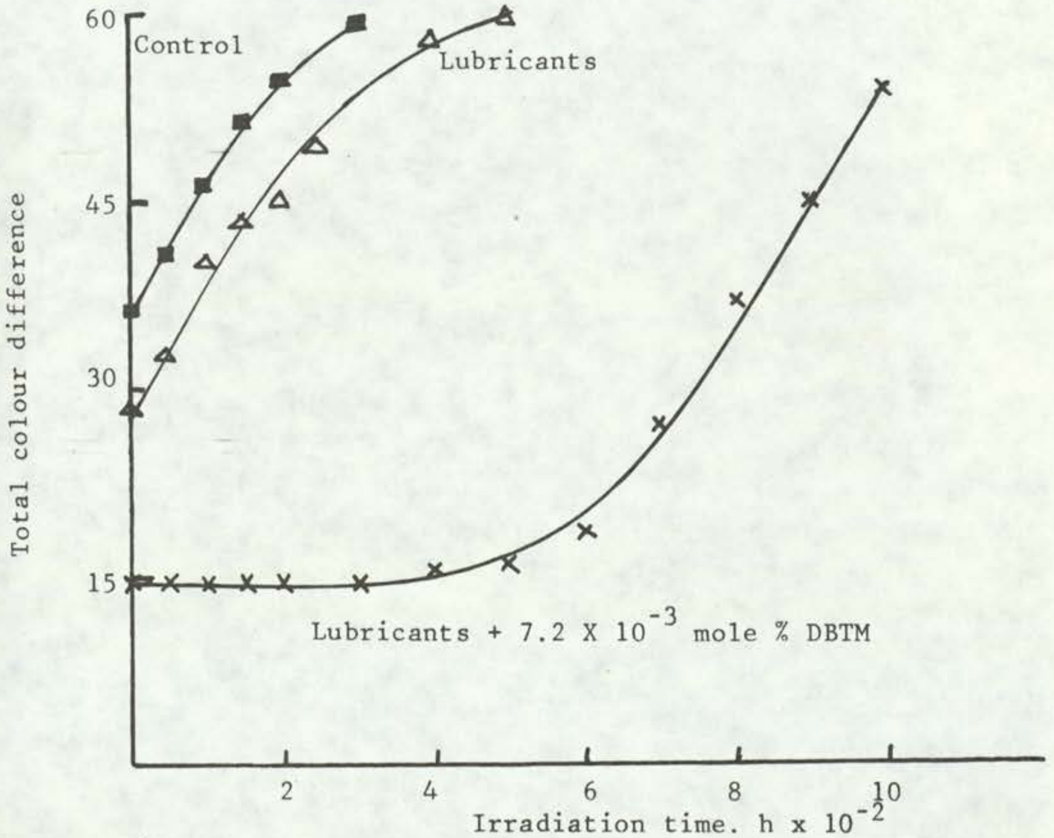


Fig. 3.47: Effect of uv irradiation on colour formation in PVC. Samples processed at 180°C for 6 min.

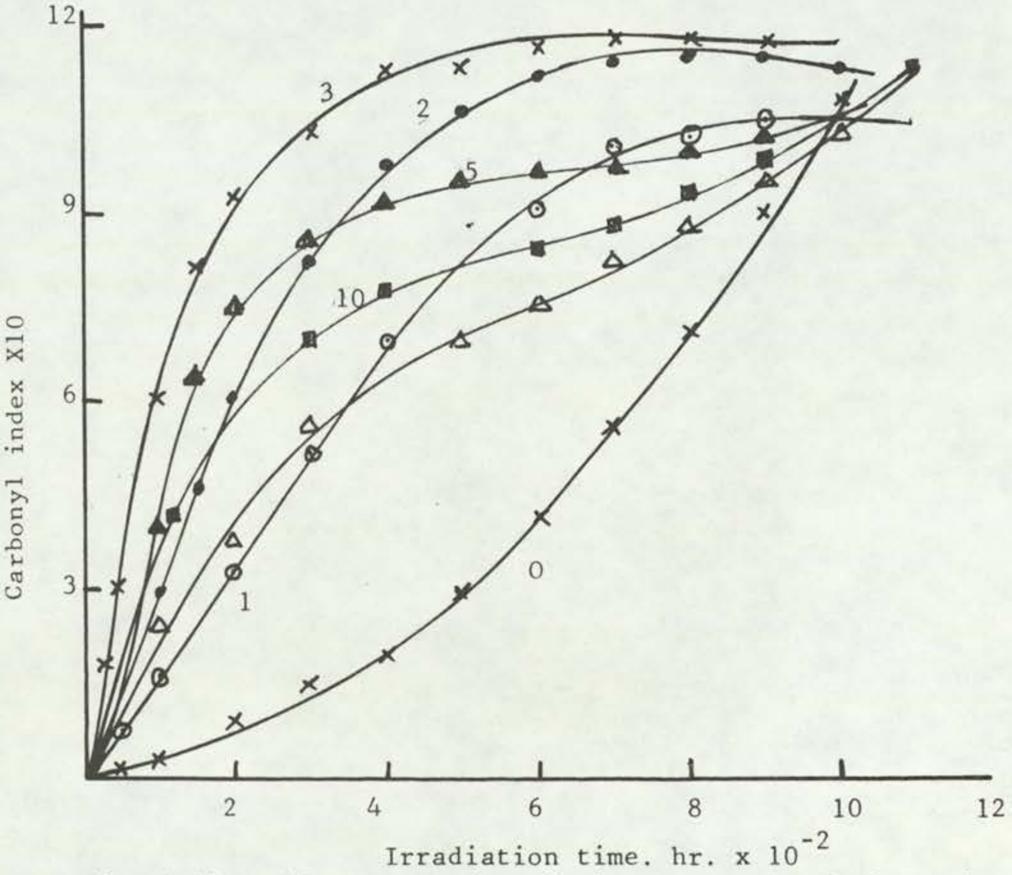


Fig. 3.48: Effect of uv irradiation on carbonyl formation in unstabilised PVC. Numbers on the curves represent processing time. (min) at 180°C.

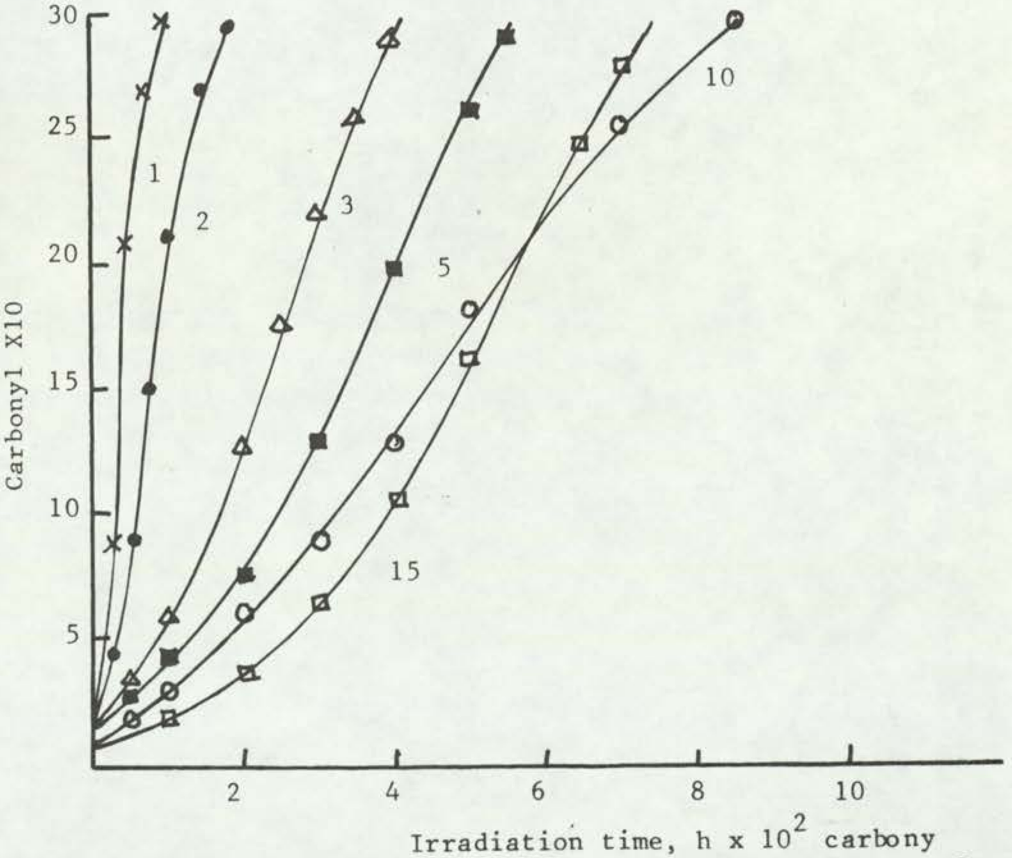


Fig. 3.49: Effect of uv irradiation on hydroxyl group formation in the gel phase of PVC. Numbers on curves represent processing time (min, 180°C)

processing after which the carbonyl decreases with increasing severity of the processing operation. This observation corresponds very well with the fact that chain rupture of polymer molecules are highest in the first minutes of mechanochemical degradation[27,28] when the polymer is still in the solid or partially molten state. The resultant macroalkyl radicals will react rapidly with available oxygen to form alkylperoxyl radicals which will ultimately give rise to hydroperoxides through hydrogen abstraction. It is anticipated that these peroxidic groups incorporated into the polymer during the processing operation are finally converted into carbonyl compounds and as such the thermal history of the polymer may well explain the observed results in fig. 4.48.

The photo-oxidation of the gel phase representing the dichloromethane-insoluble fraction of the polymer is shown in fig. 3.49. Carbonyl formation is higher in the early stage of processing (1 and 2 min) and decreases thereafter with increasing processing time. Peroxide intermediates formed during processing may contribute to this behaviour. The soluble fraction of processed samples is found to accelerate photo-oxidative formation of carbonyl index in unprocessed samples (fig.3.50), and this indicates the presence of photo-initiating irregularities in the processed fraction.

The effect of irradiation on hydroxyl index in PVC is shown in fig. 3.51 while the photo-oxidation of the gel phase is shown in fig. 3.52. Both results indicate that mildly processed samples photo-oxidise more rapidly than severely processed samples possibly as a result of higher

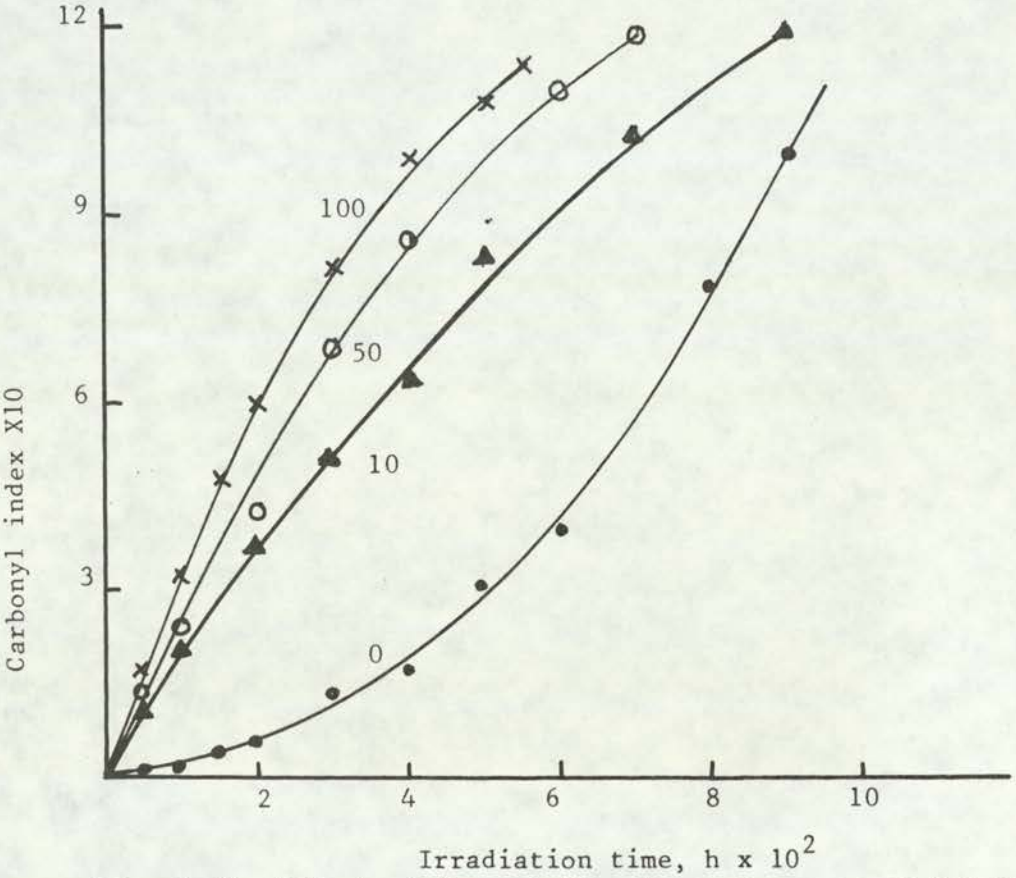


Fig. 3.50: Effect of the soluble phase of processed PVC (10 min, 180°C) on carbonyl formation during uv irradiation. Numbers on curves represent percentage of processed phase.

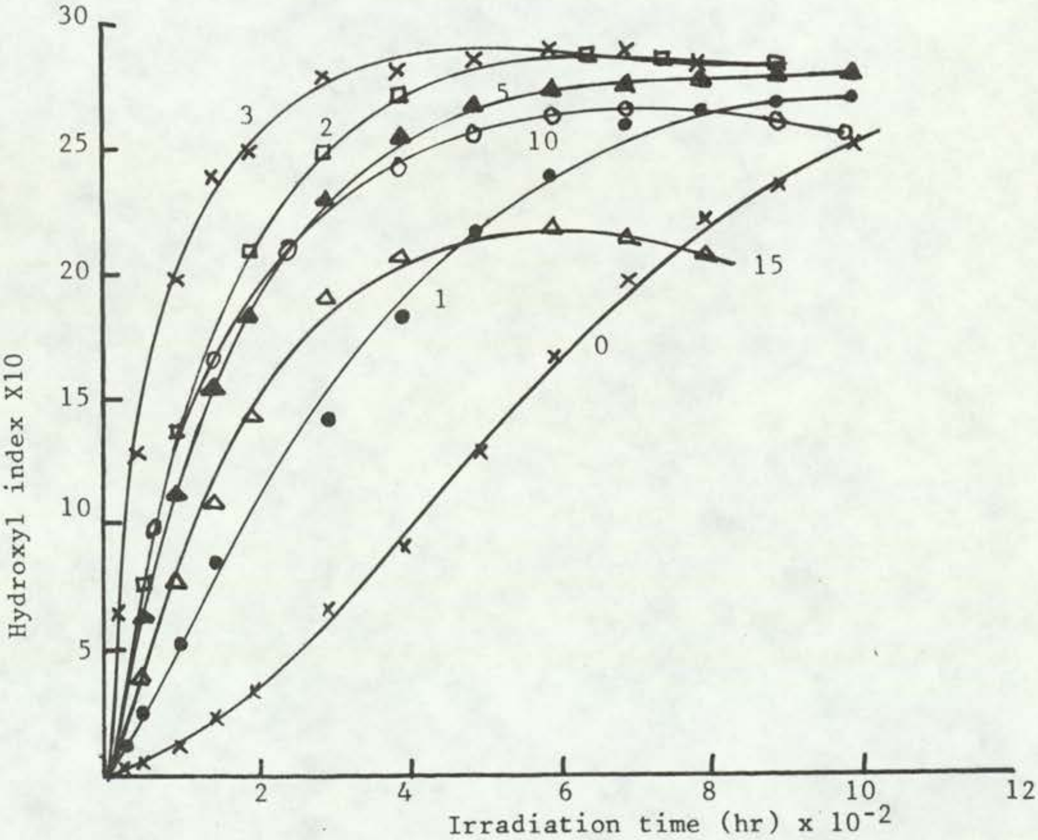


Fig. 3.51: Effect of uv irradiation on hydroxyl group in unstabilised PVC. Numbers on the curves represent processing time(min) at 180°C.

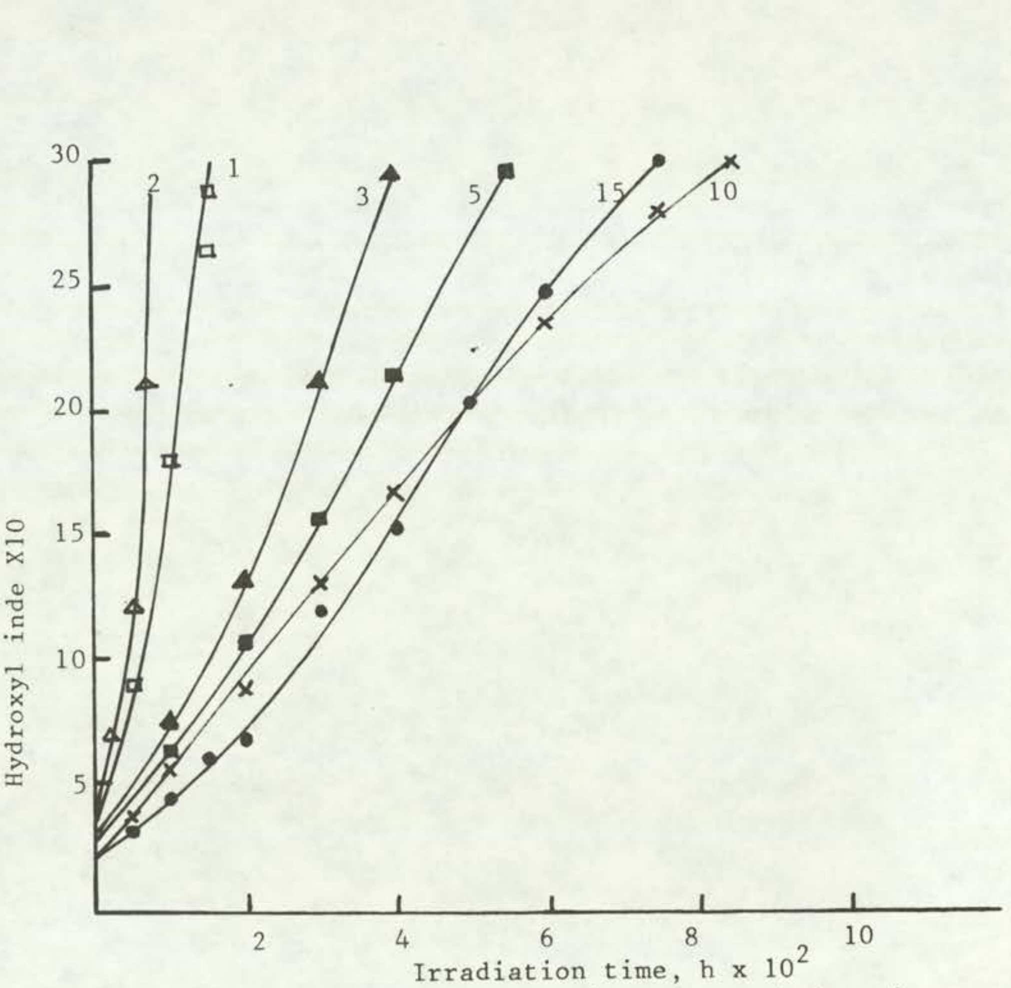


Fig. 3.52: Effect of preprocessing time on hydroxyl group formation in PVC during uv irradiation. Numbers on curves represent processing time (min) at 180°C.

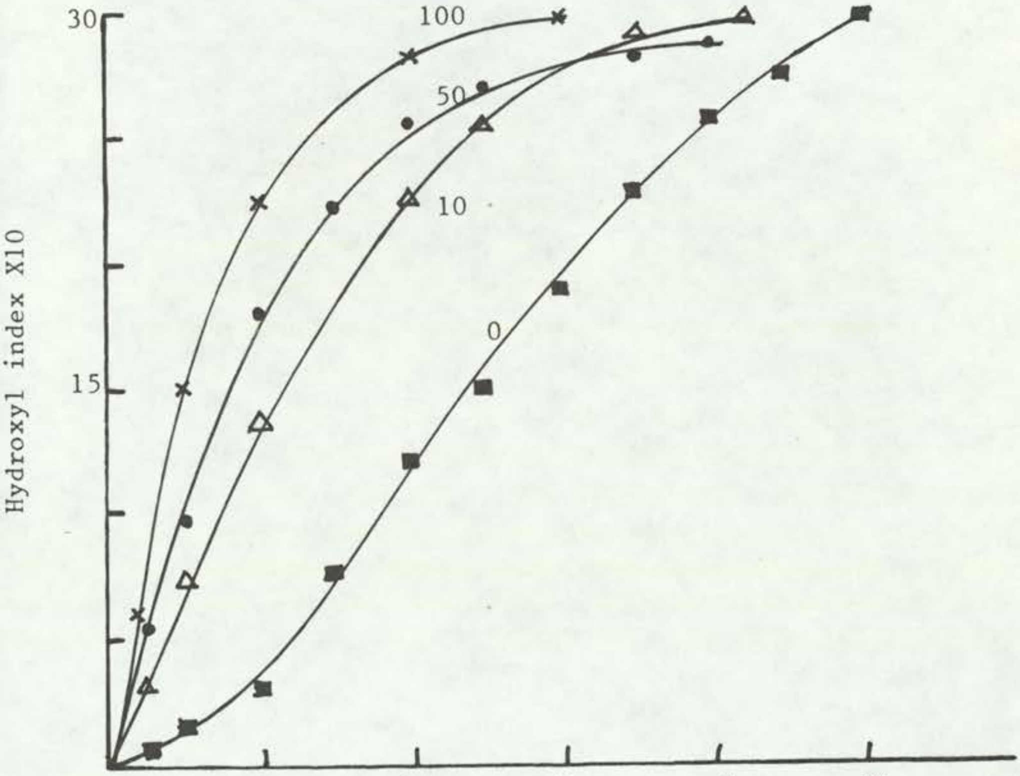


Fig. 3.53: Effect of the soluble phase of processed PVC (180°C, 10 min) on hydroxyl group formation in unprocessed sample. Numbers on the curves represent percentage of processed phase.

peroxides present in the former samples. It can be seen in fig. 3.53 that the presence of the soluble phase of processed samples increases the rate of photo-oxidation of unprocessed samples, the accelerating effect increases with increasing concentration of the processed material in the formulation. This is a further evidence that processing decreases the photo-oxidative stability of the polymer.

CHAPTER FOUR

EFFECT OF DIBUTYLTIN MALEATE, LEAD STEARATE AND PHENOLIC ANTIOXIDANTS ON THE PROCESSING, THERMAL AND PHOTO-OXIDATIVE STABILITY OF PVC.

4.1 Experimental Procedure

PVC formulations were processed at 180°C in the presence of DBTM and a lubricant mixture consisting of 0.65% Wax E and 0.8% CaSt. The effect of partial replacement of DBTM by commercial phenolic antioxidants Irganox 1300, 1076 and 1010 on the melt- and thermal oxidative stability of PVC was investigated. Lead stearate (PbSt) was also investigated as a thermal stabiliser of PVC. The processed polymer was compression moulded into films and examined for processing, thermal and photo-oxidative stability as described in Chapter 2.

4.2 Effect of Stabilisers during Processing

4.2.1 Effect of DBTM and PbSt

The effect 2.9×10^{-3} mole % DBTM and PbSt without lubricants on both the maximum and minimum torque generated in PVC during processing is shown in fig. 4.1. The highest torque levels are observed in control samples without stabilisers. Lower levels of torque are observed in formulations containing PbSt than those of DBTM. This indicates a superior lubricating effect of PbSt than DBTM and hence a reduced mechanical shear of the polymer chains in samples formulated with PbSt.

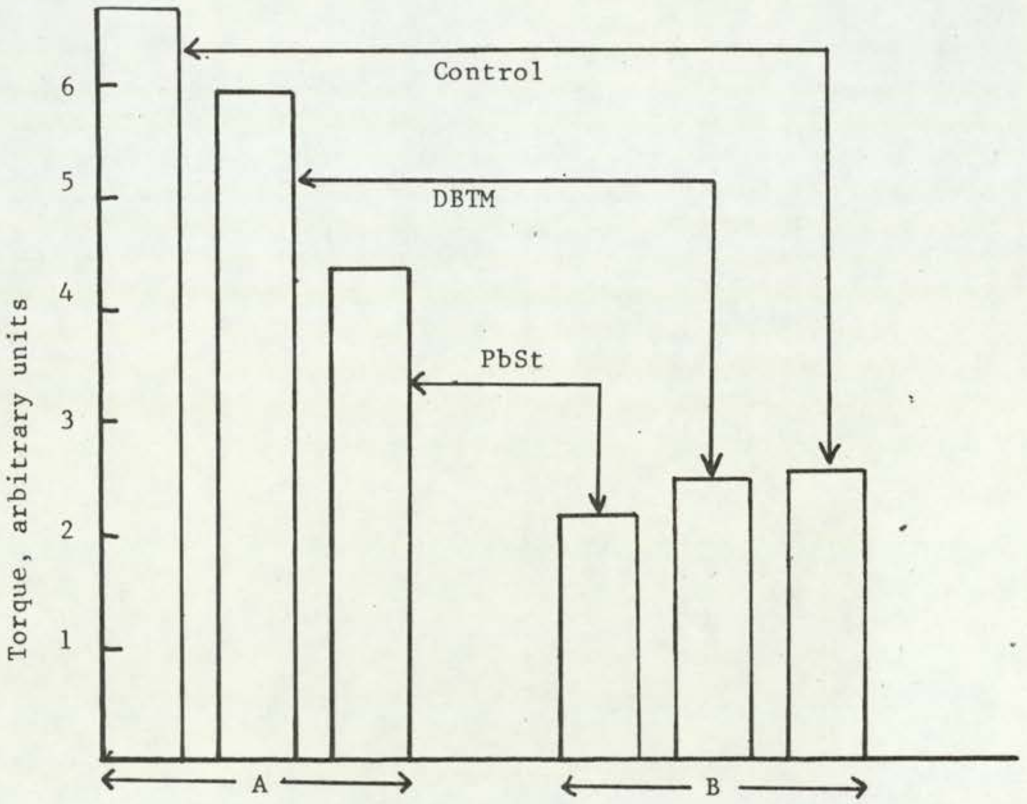


Fig. 4.1: Effect of DBTM and PbSt on both the initial torque maxima at the onset of processing (A) and on the torque at equilibration (B) Formulations without lubricants.

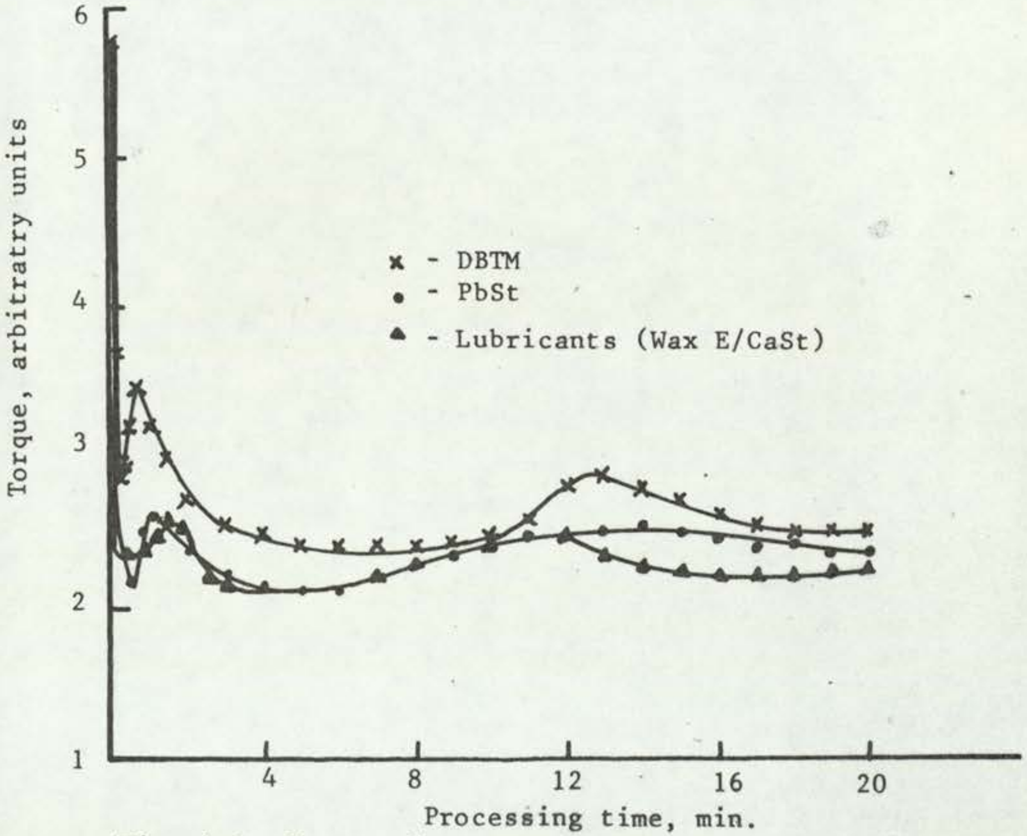


Fig. 4.2: Changes in the torque generated in PVC during thermal processing at 180°C; a comparison of the effect of DBTM and PbSt with lubricants.

Figure 4.2 shows the changes in the torque generated in PVC during processing and compares the effect of DBTM and PbSt with the Wax E/CaSt lubricant system.

The total colour difference, measured by Colour Master Model V, formed in PVC is as shown in fig. 4.3. Colour formation is highest in the control sample in which there is an initial rapid colour development up to 3 min, followed by a slower linear rate of colour formation. A similar result was reported earlier by Cooray.[67,141]. In the presence of 2.9×10^{-3}mole % PbSt and DBTM, it is found that colour formation is lower with PbSt than with DBTM during the first 10 min. of processing after which DBTM gives a better colour stability than PbSt. It is known[28] that mechanical shearing accounts principally for the initiating impurities in the early stages of processing when the polymer is melting. In contrast to this initial stage where thermal degradation plays a minor role, the latter stages are primarily thermal-oxidative in nature. The crossover in the activity of PbSt and DBTM in reducing colour formation in PVC may therefore be related to a change from a mechanical degradation stage when PbSt functions as a better lubricant to a purely thermal oxidative degradation stage when DBTM becomes the more effective stabiliser. However at higher concentrations of 5.8 and 7.2×10^{-3} mole % colour formation is lower with PbSt than with DBTM and the crossover observed at 2.9×10^{-3} mole % is absent (fig. 4.4 and 4.5).

The curves for the chemically determined unsaturation are shown in figs. 4.6-4.8. It can be seen that the shape of these curves are similar to those of the total colour difference demonstrating a striking

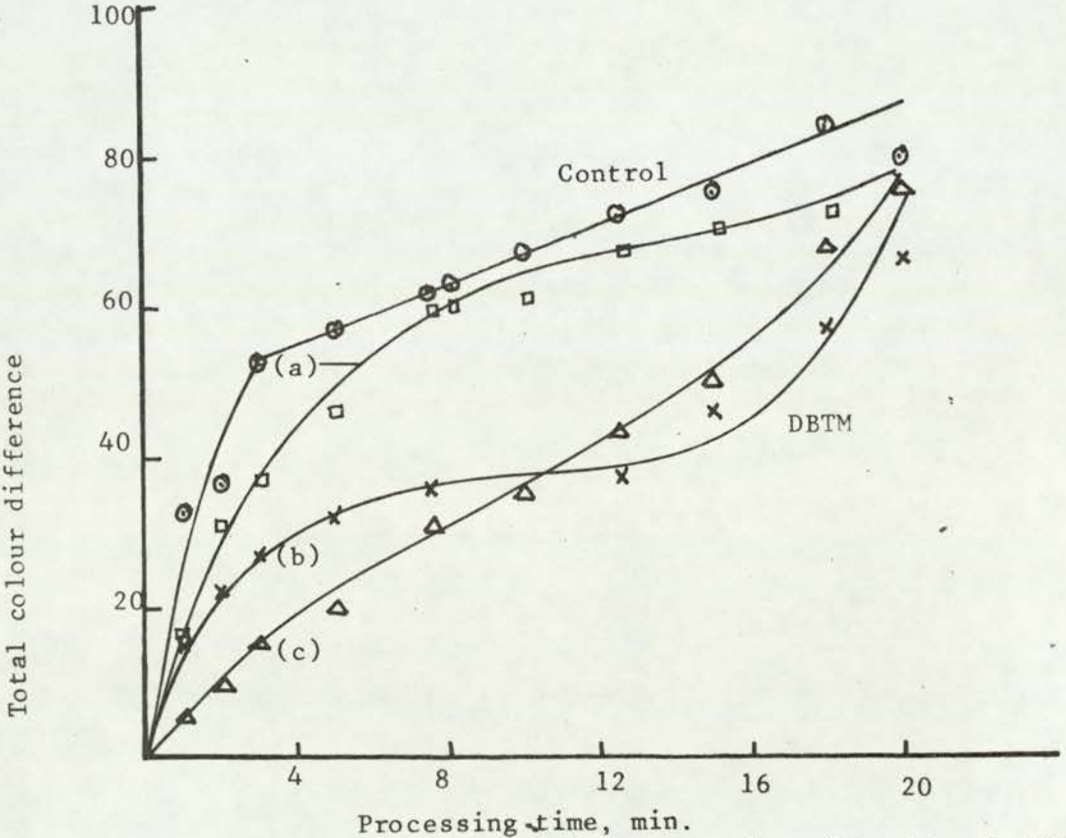


Fig. 4.3: Effect of stabilisers on colour formation in PVC during thermal processing at 180°C. (a) Lubricants (b) 2.9 x 10^{-3}M DBTM; (c) 2.9 x 10^{-3}M PbSt.

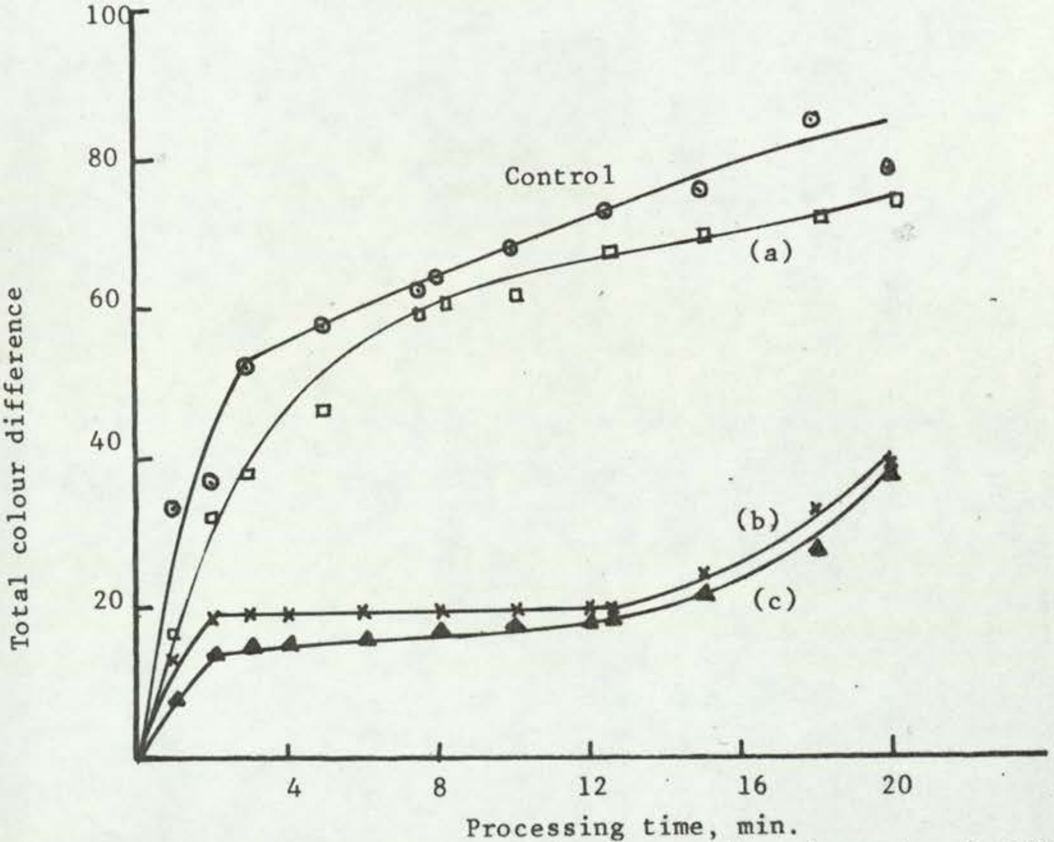


Fig. 4.4 Effect of stabilisers on colour formation in PVC during thermal processing at 180°C, (a) Lubricants; (b) 5.8 x 10^{-3}M DBTM; (c) 5.8 x 10^{-3} M PbSt, b,c with lubricants

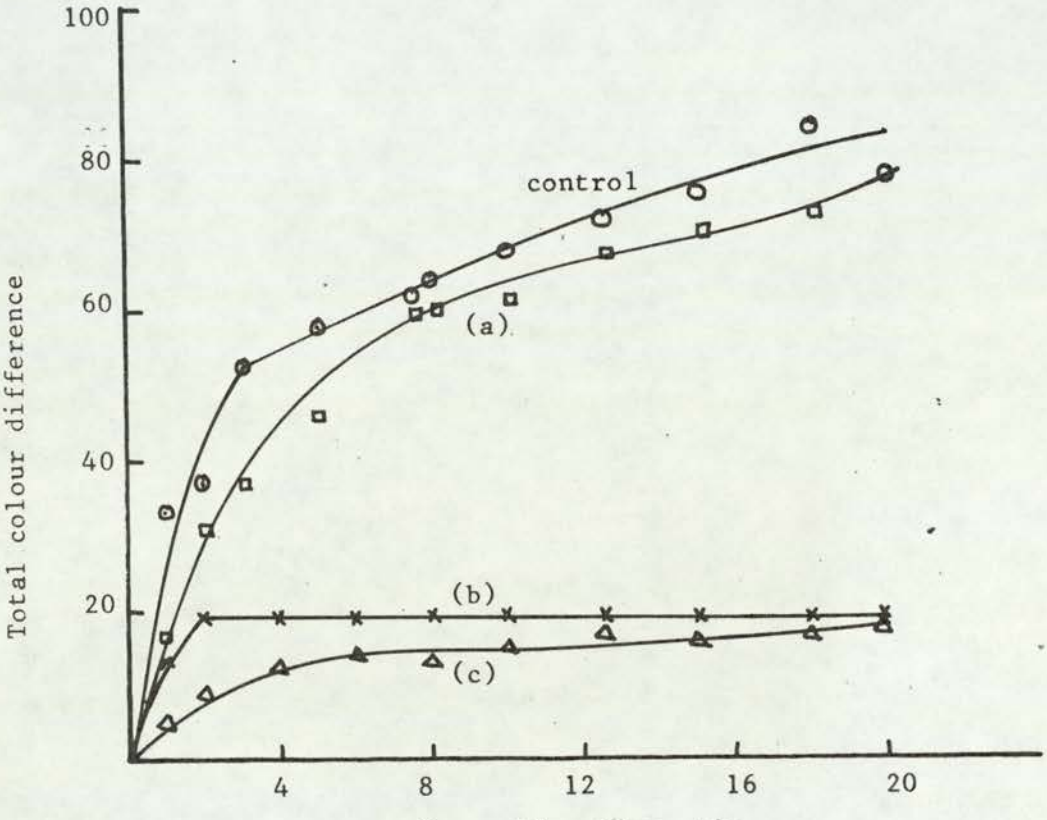


Fig. 4.5: Effect of stabilisers on colour formation in PVC during thermal processing at 180°C. (a) Lubricants; (b) 7.2 x 10^{-3}M DBTM; (c) 7.2 x 10^{-3}M PbSt. b,c with lubricants.

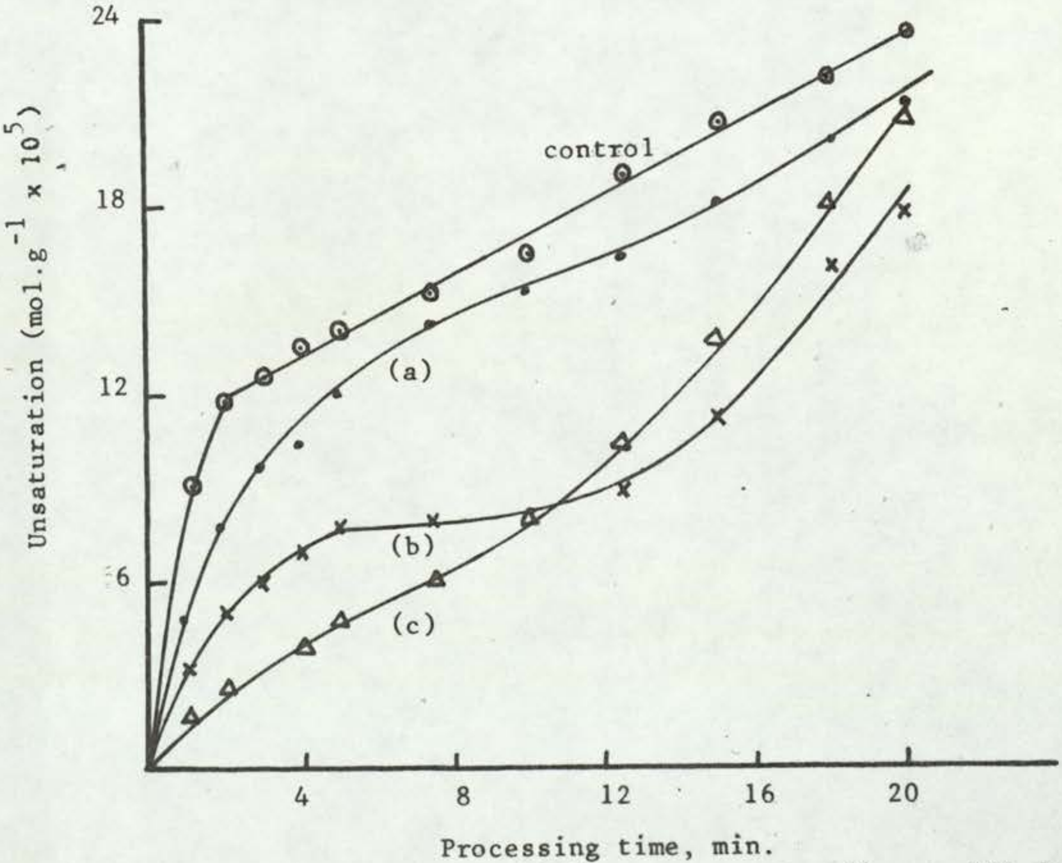


Fig. 4.6: Effect of stabilisers on unsaturation in PVC during thermal processing at 180°C. (a) lubricants; (b) 2.9 x 10^{-3}M DBTM; (c) 2.9 x 10^{-3}M PbSt. b,c with lubricants.

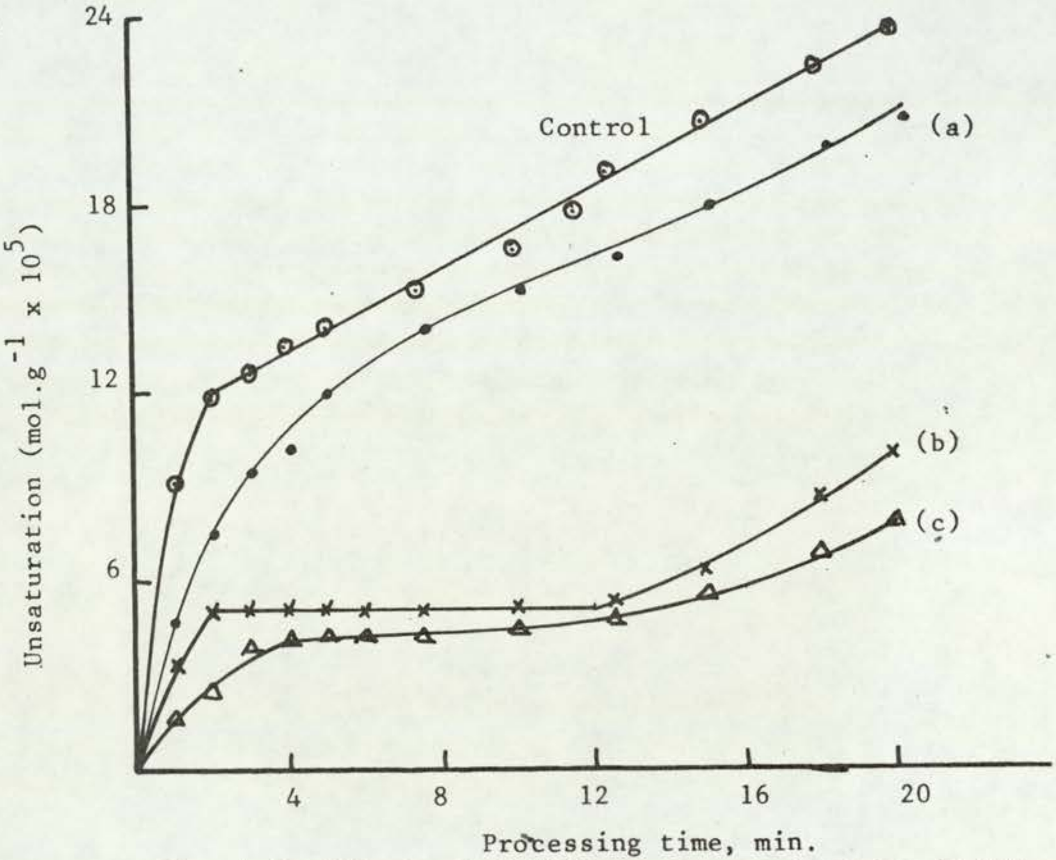


Fig. 4.7: Effect of stabilisers on unsaturation in PVC during thermal processing at 180°C. (a) lubricants; (b) 5.8x 10^{-3} mole% DBTM (c) 5.8 x 10^{-3}M PbSt.

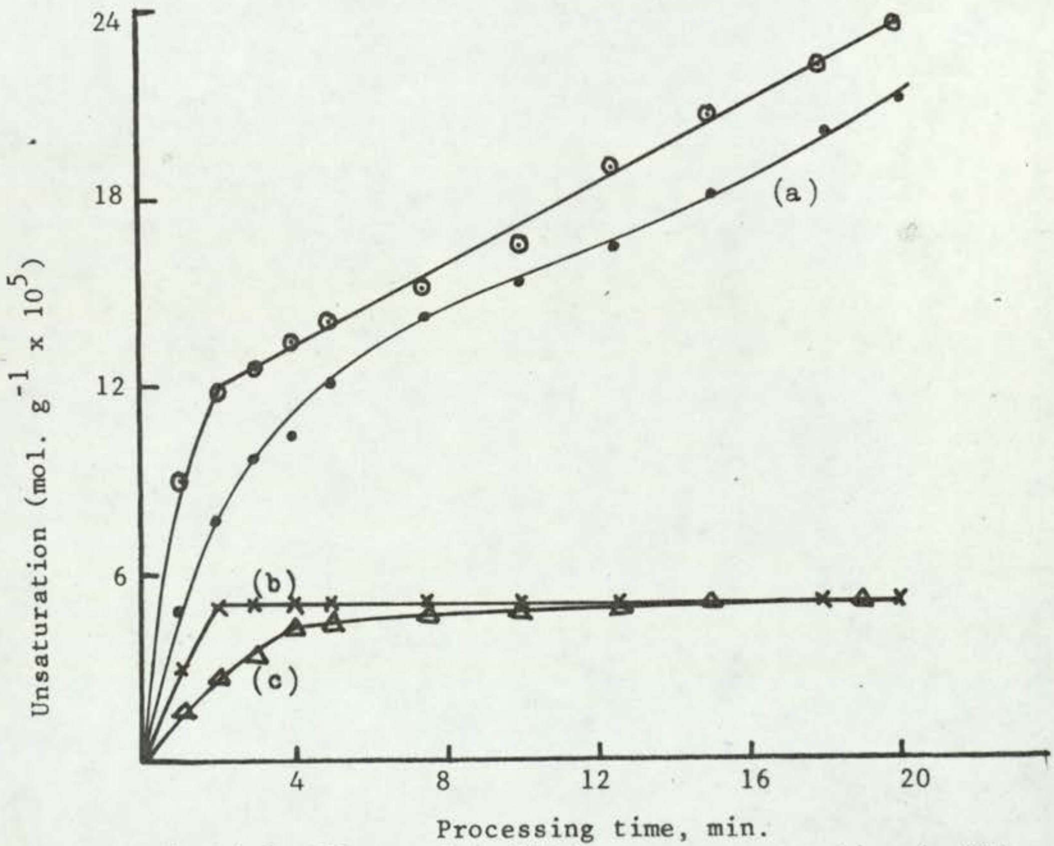


Fig. 4.8: Effect of stabilisers on unsaturation in PVC during thermal processing at 180°C. (a) lubricants; (b) 7.2 x 10^{-3} mole % DBTM (c) 7.2 x 10^{-3} M PbSt.

correlation between these measurements. The concentration of unsaturation is found to be highest in the unstabilised sample (control) while both DBTM and PbSt show concentration dependent stabilising effects (figs. 4.6-8). Lubricants lowered the formation of both unsaturation and total colour difference but they are much less effective than DBTM and PbSt.

4.2.2 Effect of DBTM and PbSt in combination with Phenolic Antioxidants

Phenolic antioxidants were incorporated into PVC formulations to serve, possibly, as synergists with DBTM and PbSt under thermal oxidative conditons since these antioxidants are known to act by the chain-breaking donor (CB-D) antioxidant mechanism by donating their phenolic protons to alkylperoxyl radicals.[44,47] Since the polymer samples investigated under thermal oxidative conditions (oven ageing at 140°C) were actually preprocessed at 180°C, the effect of the phenolic antioxidants in combination with DBTM and PbSt on the melt stability of the polymer was also investigated.

The effect of PbSt alone at 2.9 and 5.8×10^{-3} mole % and in combination with phenolic antioxidants at $(2.9/2.9) \times 10^{-3}$ mole % was investigated. Figures 4.9 and 10 show the total colour difference and unsaturation in PVC formulated with PbSt alone and in combination with Irganox 1300. A comparison of curves c with d in both figs. 4.9 and 10 shows that the partial replacement of PbSt by Irg. 1300 reduces the processing stability of PVC and this may be due to the inability of Irg.1300 to scavenge hydrogen chloride liberated during processing. The effect of

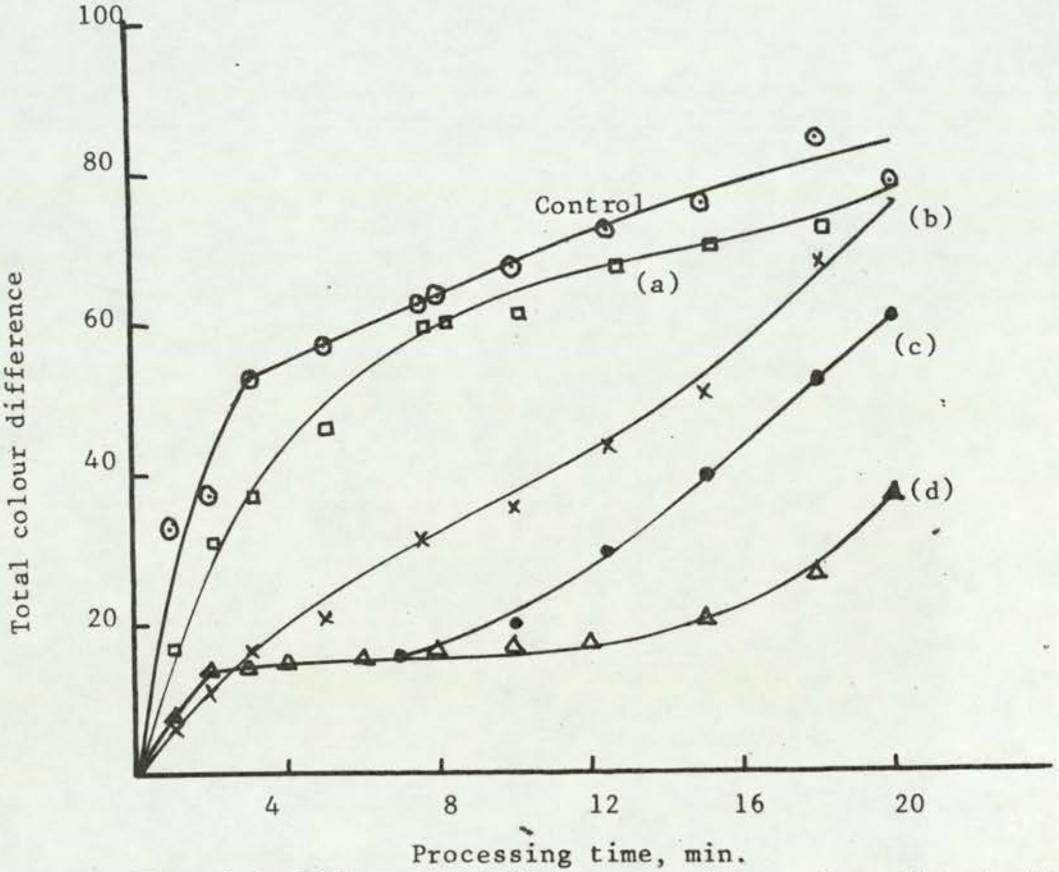


Fig. 4.9: Effect of stabilisers on colour formation in PVC during thermla processing at 180°C (a) lubricants; (b) 2.9 x 10^{-3}M (PbSt; (c) PbSt + Irg. 1300 (2.9:2.9): (d) 5.8x 10^{-3} M PbSt, (b-d contain lubricants)

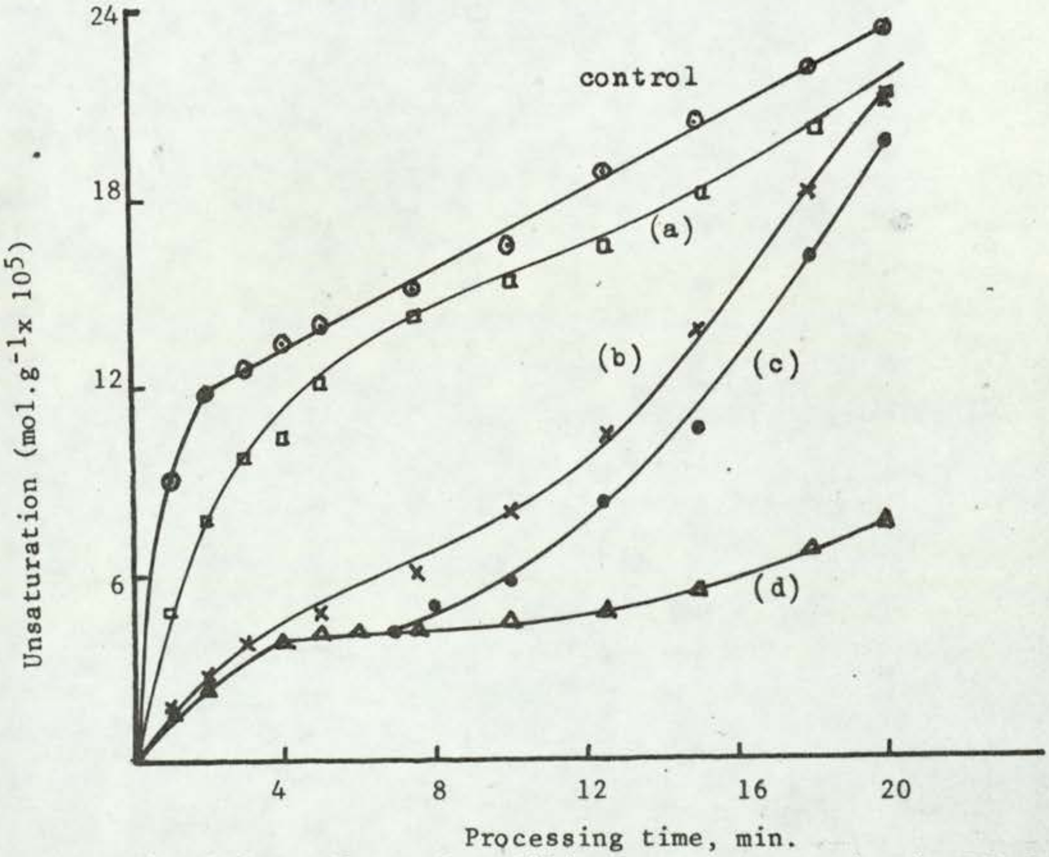


Fig. 4.10: Effect of stabilisers on unsaturation in PVC during thermal processing at 180°C. Captions (a-d) are same as in fig. 4.9.

Irganox 1076 and 1010 on total colour difference and unsaturation are similar to that of Irganox 1300 and these are shown in figs. 4.11 and 12, and 4.13 and 14 respectively.

The effect of DBTM at 2.9 and 7.2×10^{-3} mole % of phenolic antioxidants was investigated and the results obtained are shown in figs. 4.15-20. At 7.2×10^{-3} mole % DBTM, after the initial formation within the first two minutes, further formation of both unsaturation and colour are retarded as was reported previously by Vyvoda[121] and Cooray.[138] Figures 4.15 and 16 show the effect of DBTM/Irg. 1300 mixtures on colour and unsaturation and it can be seen that addition of Irg. 1300 is ineffective as a processing stabiliser in PVC. In fact, PVC samples which were processed with Irg. 1300 alone were found to produce colour and unsaturation similar to the control sample without additives, confirming the ineffectiveness of the phenolic antioxidant as a stabiliser for PVC under limited oxygen availability. The effect of the concentration of Irg. 1300 is only found to become noticeable after about 12 min. of processing. Similar results are obtained with DBTM/Irg. 1076 mixtures although in this case, colour stability is slightly higher (figs. 4.17 and 18) than with DBTM/Irg. 1300 formulations.

The effect of DBTM/Irg. 1010 mixtures on unsaturation and colour is shown in figs. 4.19 and 20. It can be seen that the addition of Irg. 1010 to DBTM causes a significant improvement in the stability of PVC to both colour formation and unsaturation (compare curve b with c, d and e). An induction period to further development of both colour and unsaturation of about 15 min. is observed with DBTM/Irg. 1010 mixtures as against about 12 min. in the case of DBTM (2.9×10^{-3} mole %) alone.

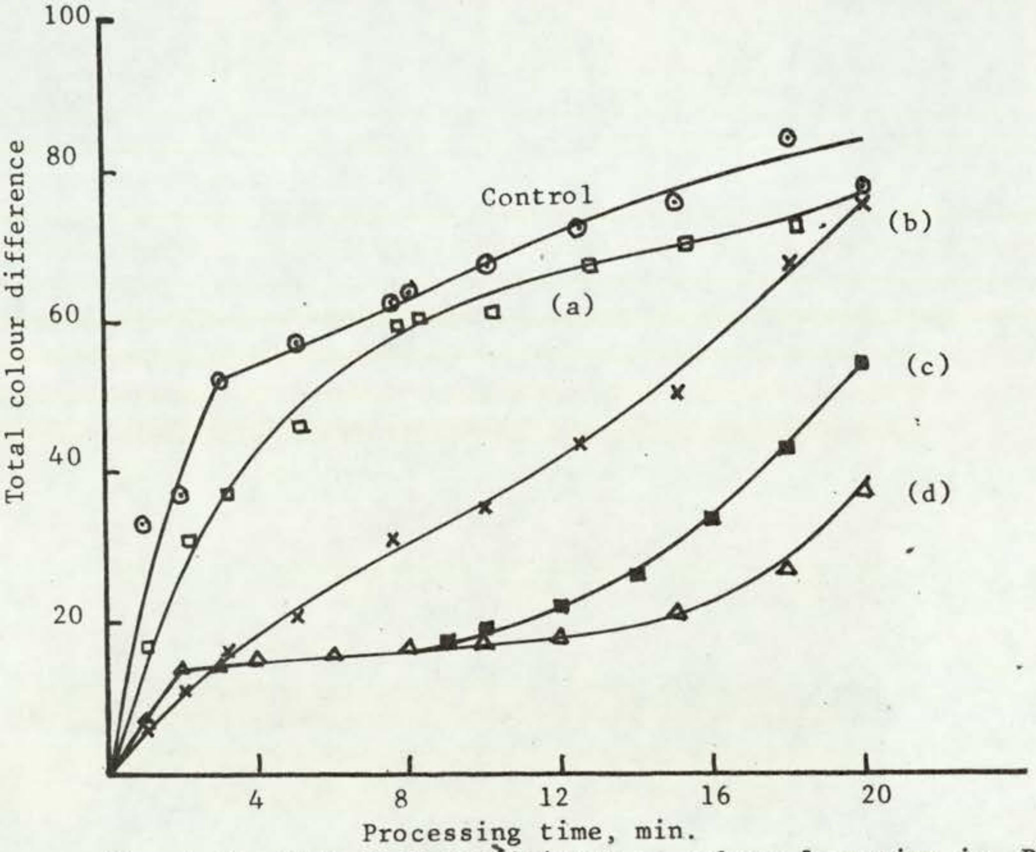


Fig. 4.11: Effect of stabilisers on colour formation in PVC during thermal processing at 180°C. (a) Lubricants; (b) 2.9 x 10^{-3}M PbSt; (c) PbSt +Irg. 1076 (2.9:2.9); (d) 5.8 x 10^{-3} M PbSt. (b-d contains lubricants).

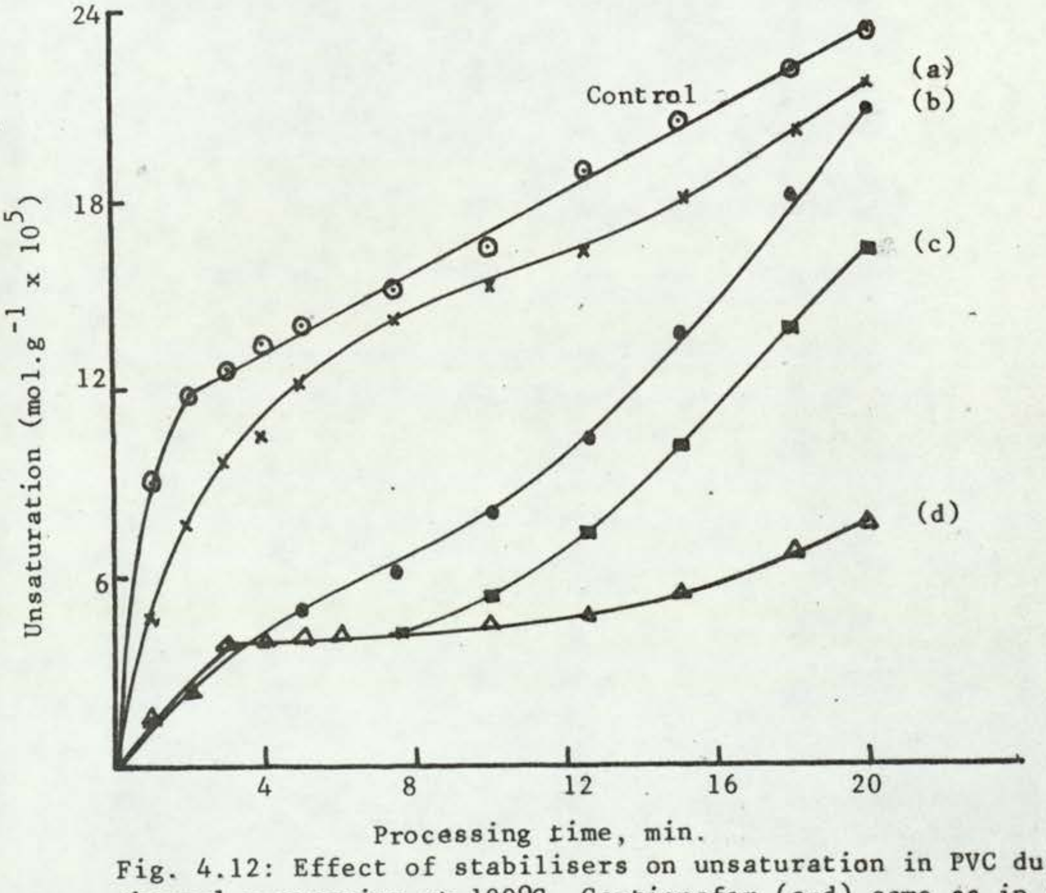


Fig. 4.12: Effect of stabilisers on unsaturation in PVC during thermal processing at 180°C. Captionsfor (a-d) same as in fig. 4.11.

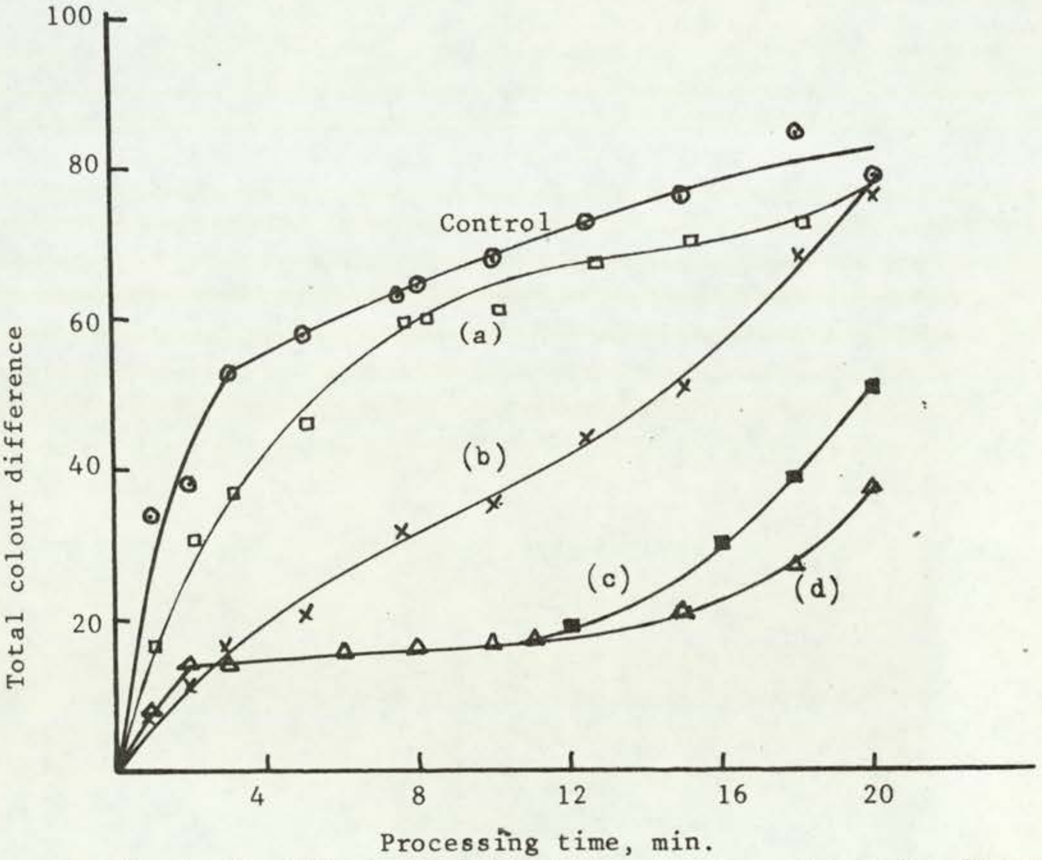


Fig. 4.13: Effect of stabilisers on colour formation in PVC during thermal processing at 180°C. (a) lubricants; (b) 2.9 x 10^{-3} mole % PbSt (c) PbSt + Irg.1010 (2.9:2.9); (d) 5.8x10^{-3} mole % PbSt. (b-d contain lubricants)

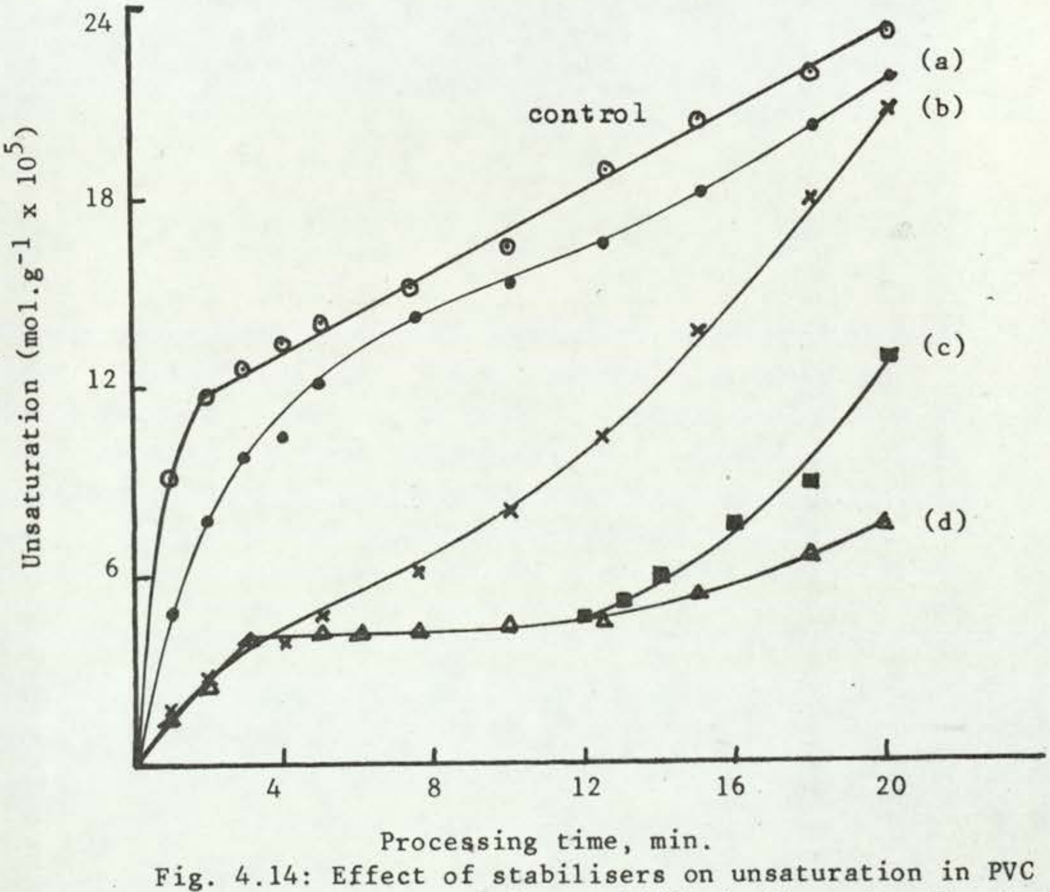


Fig. 4.14: Effect of stabilisers on unsaturation in PVC during thermal processing at 180°C (a-d) as in fig. 4.13.

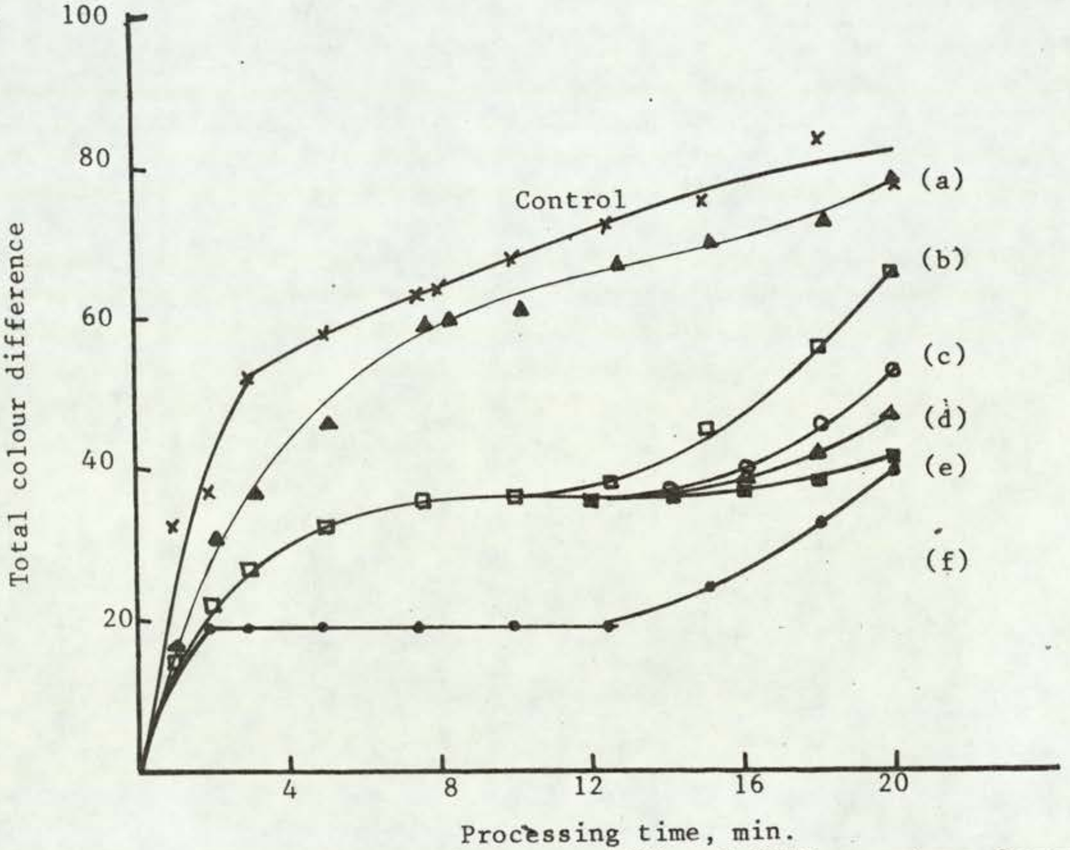


Fig. 4.15: Effect of Irganox 1300 and DBTM on colour formation in PVC during thermal processing (a) lubricants; (b) 2.9×10^{-3} DBTM; (c) DBTM + Irg. 1300 (2.9:1); (d) DBTM + Irg.1300 (2.9:2) (e) DBTM + Irg.1300 (2.9:3); (f) 5.8×10^{-3} mole% DBTM. (b-f contain lubricants).

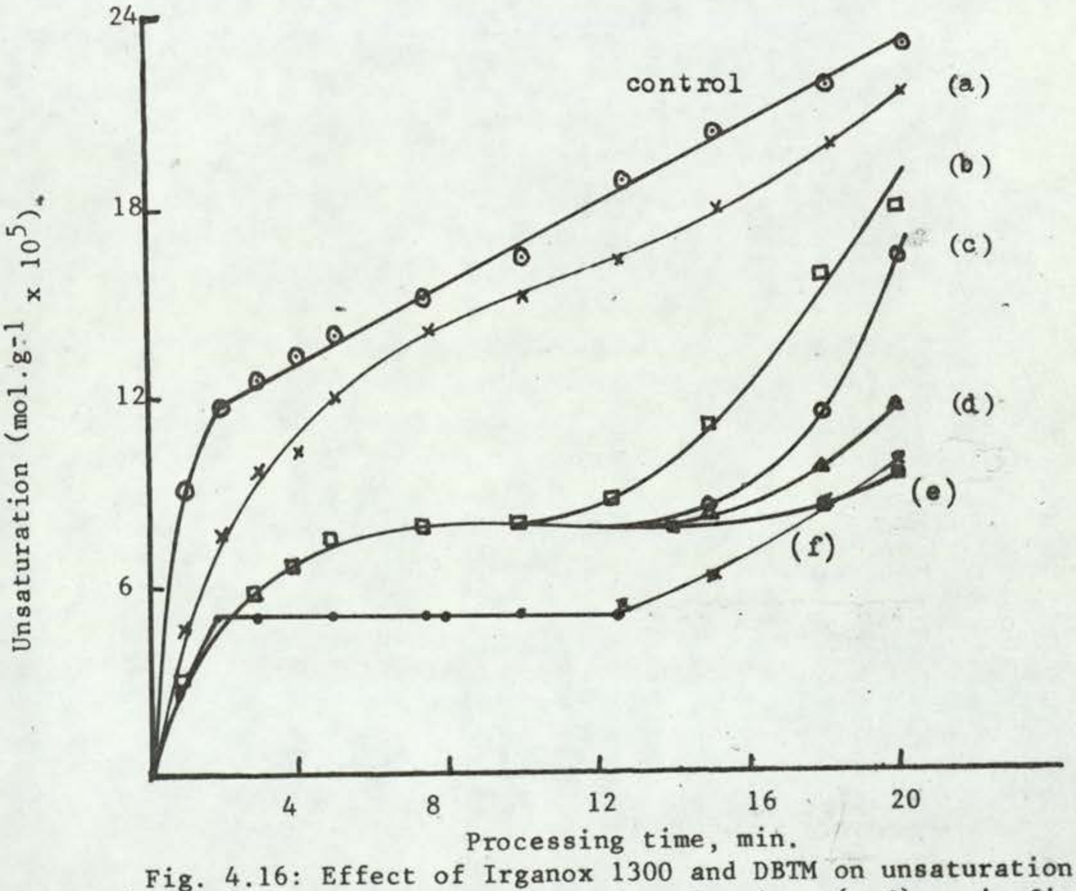


Fig. 4.16: Effect of Irganox 1300 and DBTM on unsaturation in PVC during thermal processing. Captions (a-f) as in fig. 4.15.

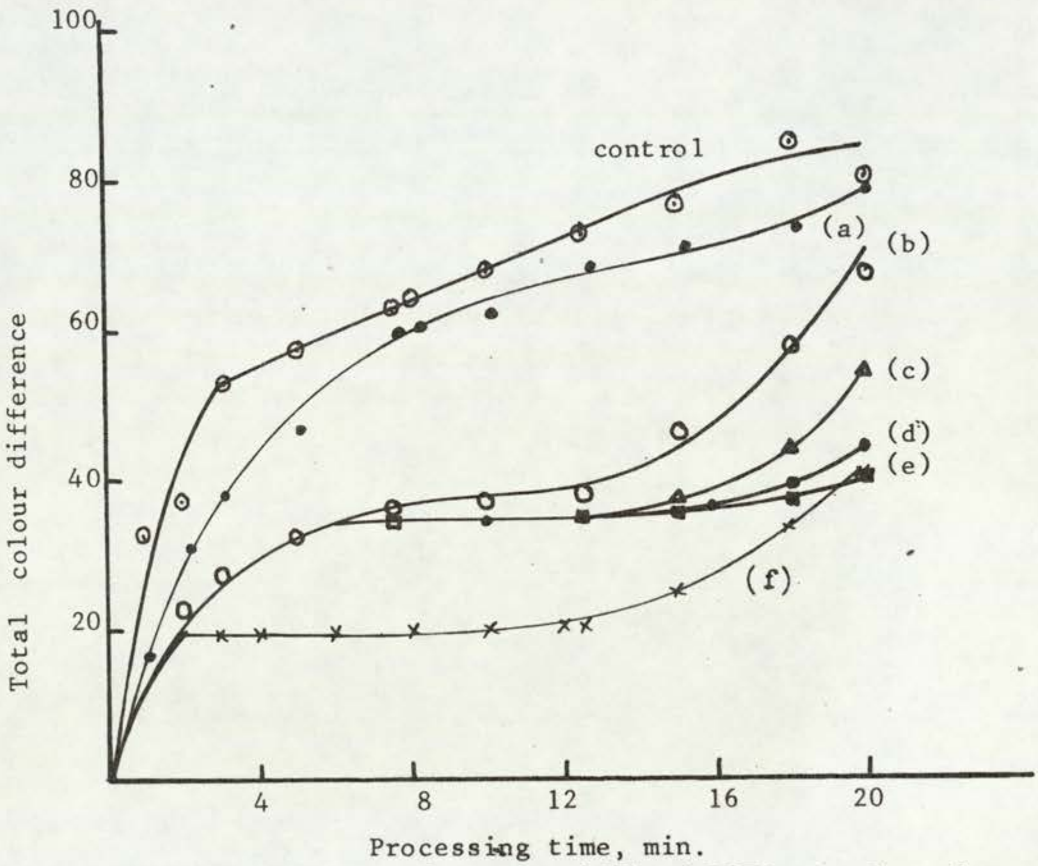


Fig. 4.17: Effect of Irganox 1076and DBTM on colour formation in PVC during thermal processing at 180°C (a) lubricants;(b) 2.9x10^{-3}M DBTM; (c) DBTM+Irg.1076 (2.9:1); (d) DBTM+Irg.1076 (2.9:2); (e) DBTM+Irg. 1076 (2.9:3); (f) 5.8x10^{-3} mole % DBTM; **(a-f with lubricants)**

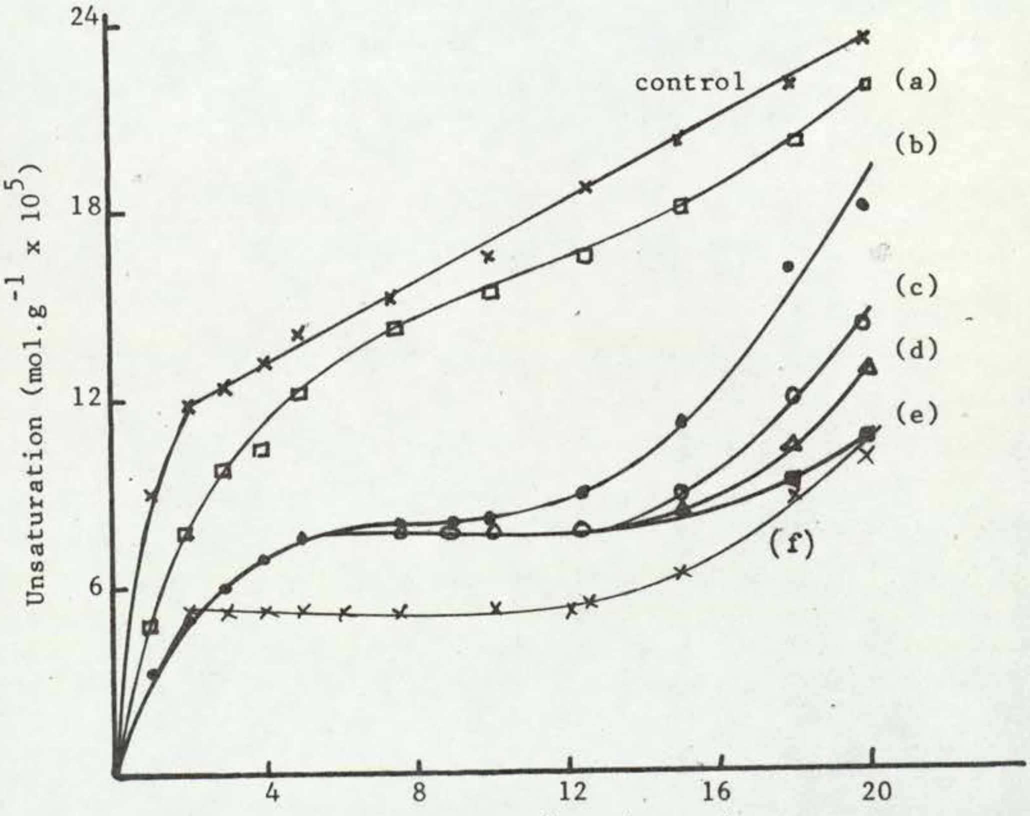


Fig. 4.18: Effect of Irganox 1076 and DBTM on unsaturation in PVC during thermal processing at 180oC (a-f) as in fig. 4.17.

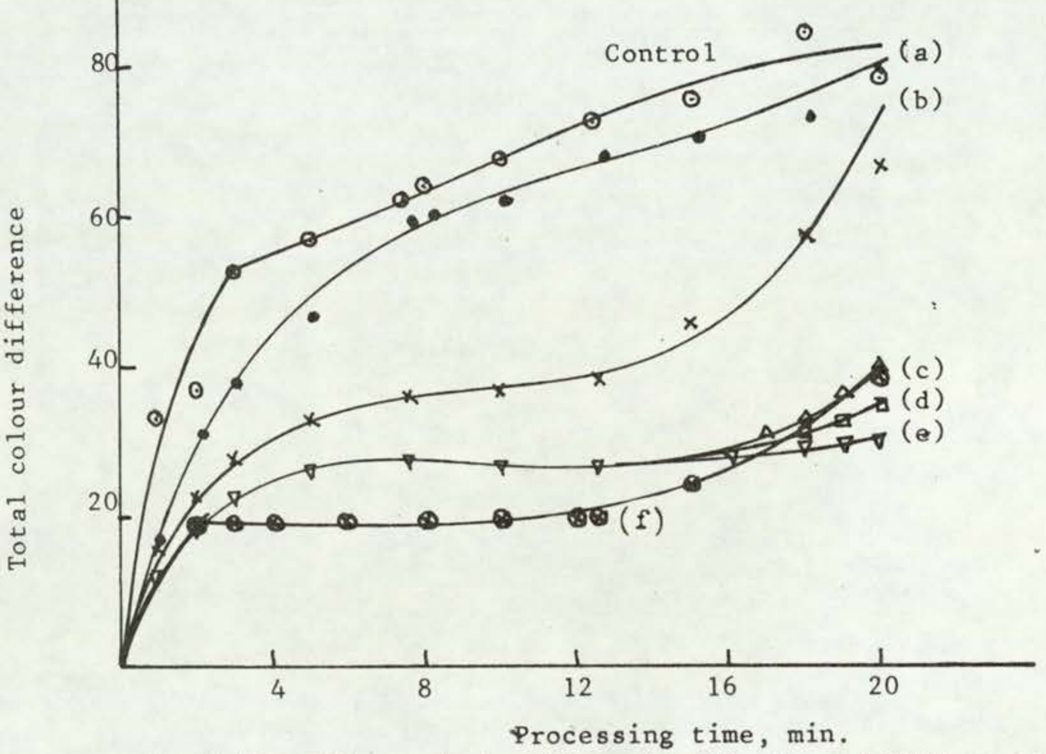


Fig. 4.19: Effect of phenolix antioxidants and DBTM on colour formation in PVC during thermal processing at 180°C (a) lubricants (b) 2.9×10^{-3}M DBTM; (c) DBTM+Irg.1010 (2.9:1); (d) DBTM + Irg.1010 (2.9:2) (e) DBTM+Irg.1010(2.9:3); (f) 5.8x10 mole %DBTM a-f with lubricants

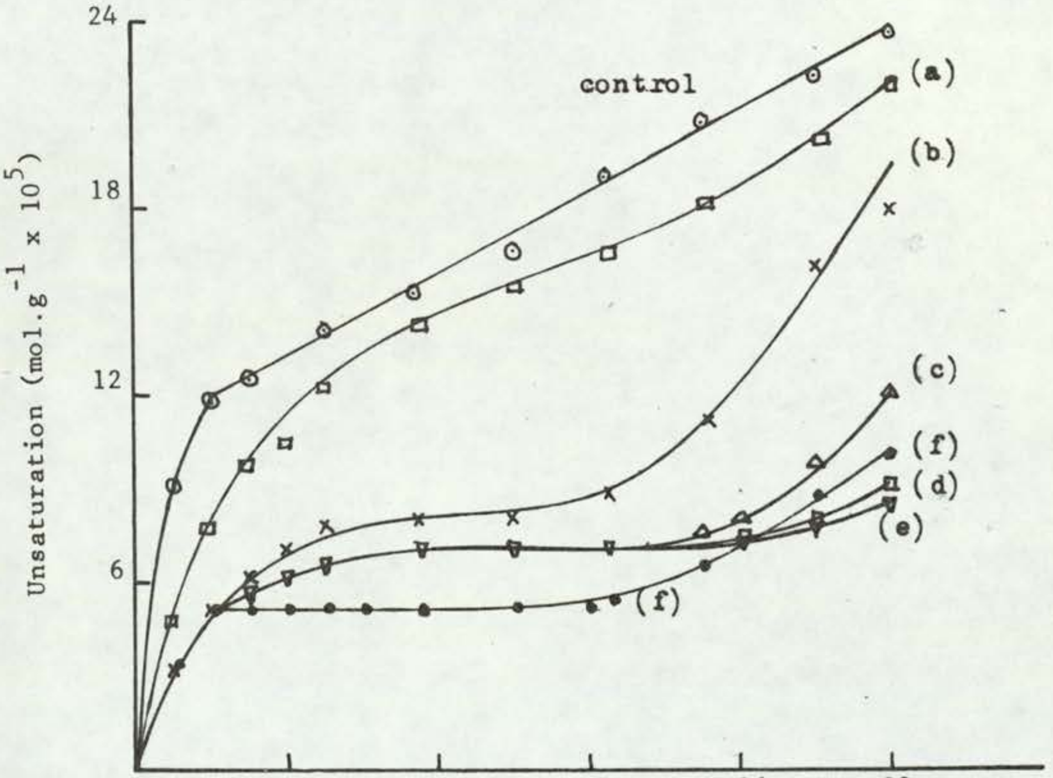


Fig. 4.20: Effect of phenolic antioxidant Irg. 1010 and DBTM on unsaturation inPVC during thermal processing at 180°C Captions (a-f) as in fig. 4.19.

Similiar to the results obtained in the presence of Irg. 1300 and 1076 (figs. 4.15-18, the effect of varying concentrations of Irg. 1010 become significant only at long periods of processing (figs. 4.19 and 20, curves c-e). The stabilising activities of Irg. 1300, 1076 and 1010 in combination with DBTM at a molar ratio of DBTM/Irg. $(5.8:1.4)x10^{-3}$ mole % are shown in figs. 4.21 and 22. It can be seen from these curves that the stabilising effectiveness of the phenolic antioxidants increases in the order Irg 1300 $\angle$ 1076 $\angle$ 1010. The reasons for this observation are discussed later.

The formation of peroxides in the control sample is compared in figs. 4.23-25 with those formed in the presence of DBTM alone and in formulations containing mixtures of DBTM and phenolic antioxidants at three different concentrations of DBTM/Irg: (2.9:2.9); (4.3:1.5); and $(5.8:4.4)x^{10-3}$ mole %. The shape of the peroxide concentration in the control sample is similar to earlier reports by Cooray and Scott[67,141] indicating two stages of peroxide accumulation. A comparison of the curves of figs. 4.23-25 with those of 4.15-20 shows that the presence of phenolic antioxidants causes a larger reduction in peroxide concentration than in colour formation and unsaturation. Increasing the total additive concentration of the DBTM/Irg. mixtures from 5.8 (fig. 4.24) to $7.2x10^{-3}$ mole % (fig 4.25) not only reduces the peroxide concentration but also increases the induction period to further peroxide accumulation. Figure 4.26 shows the effect of DBTM/Irg. mixture at $(4.3:15)x10^{-3}$ mole % on unsaturation formed in PVC.

Detailed investigation of infrared spectra was employed earlier[27] to investigate the mechanism of PVC stabilisation by DBTM. Similar studies

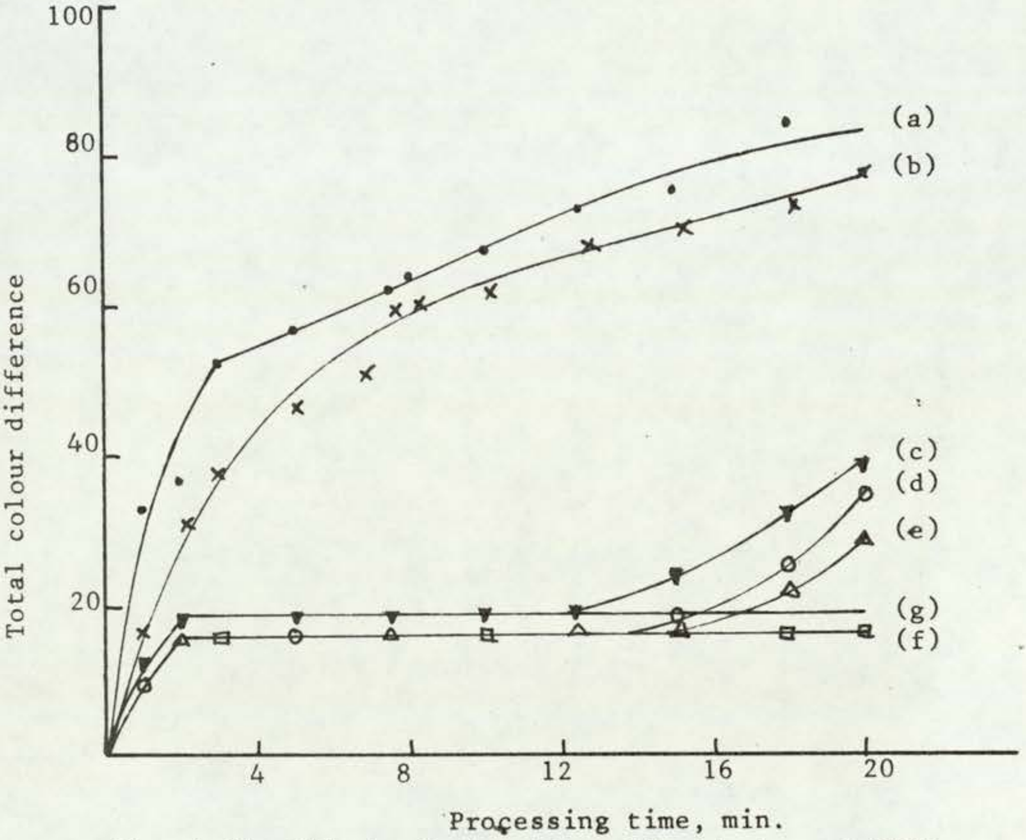


Fig. 4.21: Effect of phenolic antioxidants and DBTM on colour formation in PVC (a) control (b) Lubricants; (c) 5.8×10^{-3}M DBTM; (d) DBTM+Irg.1300; (e) DBTM+Irg.1076; (f) DBTM+Irg.1010; (g) DBTM, 7.2×10^{-3}mole %; **c-g with lubricants**

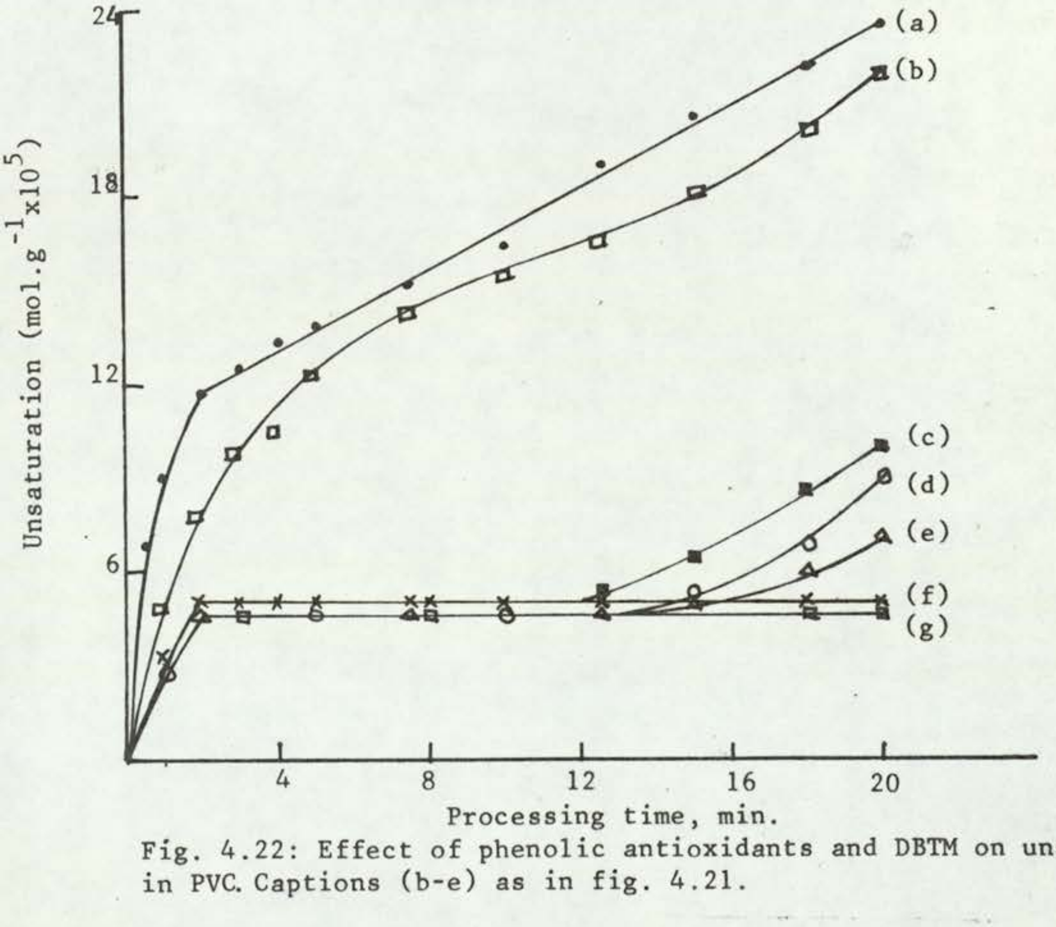


Fig. 4.22: Effect of phenolic antioxidants and DBTM on unsaturation in PVC. Captions (b-e) as in fig. 4.21.

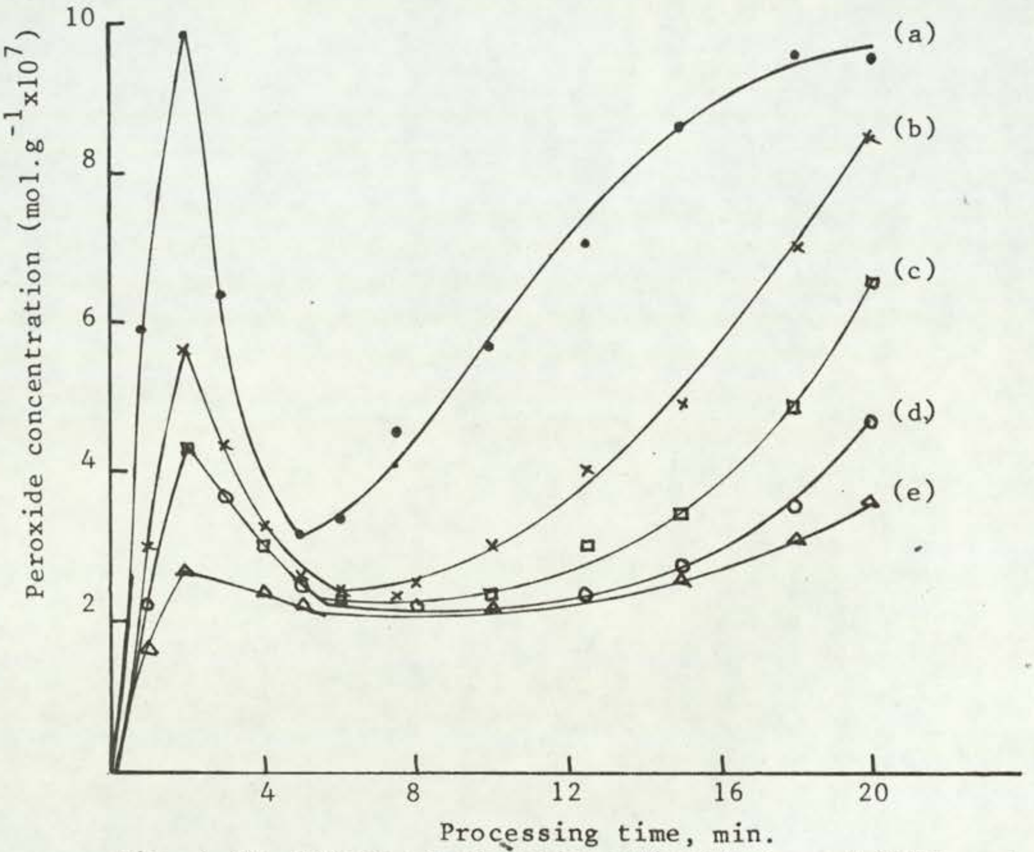


Fig. 4.23: Effect of phenolic antioxidants and DBTM on peroxide concentration in PVC during thermal processing at 180°C (a) control; (b) 2.9×10^{-3} M DBTM; (c) DBTM+Irg.1300; (d) DBTM+Irg.1076; (e) DBTM+Irg.1010, ($2.9:2.9\times10^{-3}$ mole%). b-e with lubricants.

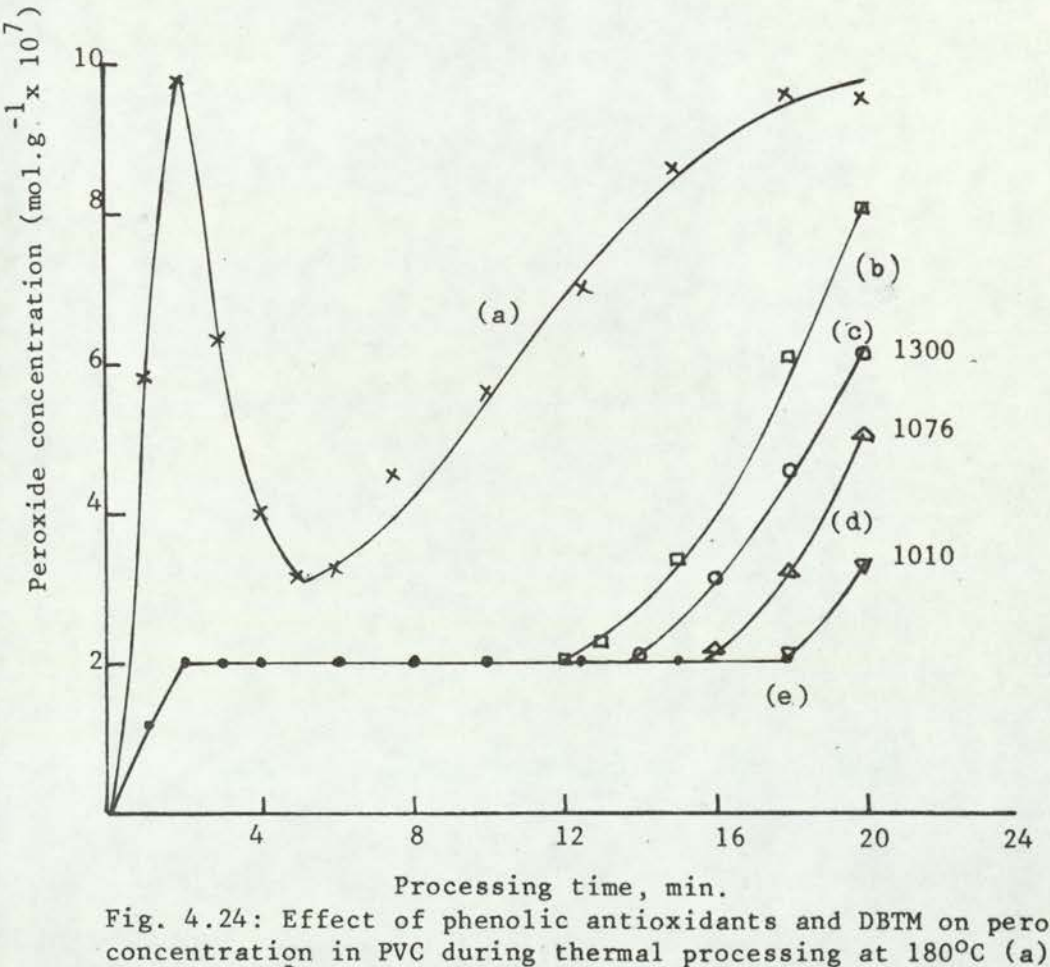


Fig. 4.24: Effect of phenolic antioxidants and DBTM on peroxide concentration in PVC during thermal processing at 180°C (a) control (b) 5.8×10^{-3}M DBTM; (c) DBTM +Irg.1300; (d) DBTM+Irg.1076 (e) DBTM+Irg.1010,$(4.3:1.5)\times10^{-3}$ mole%, b-e with lubricants.

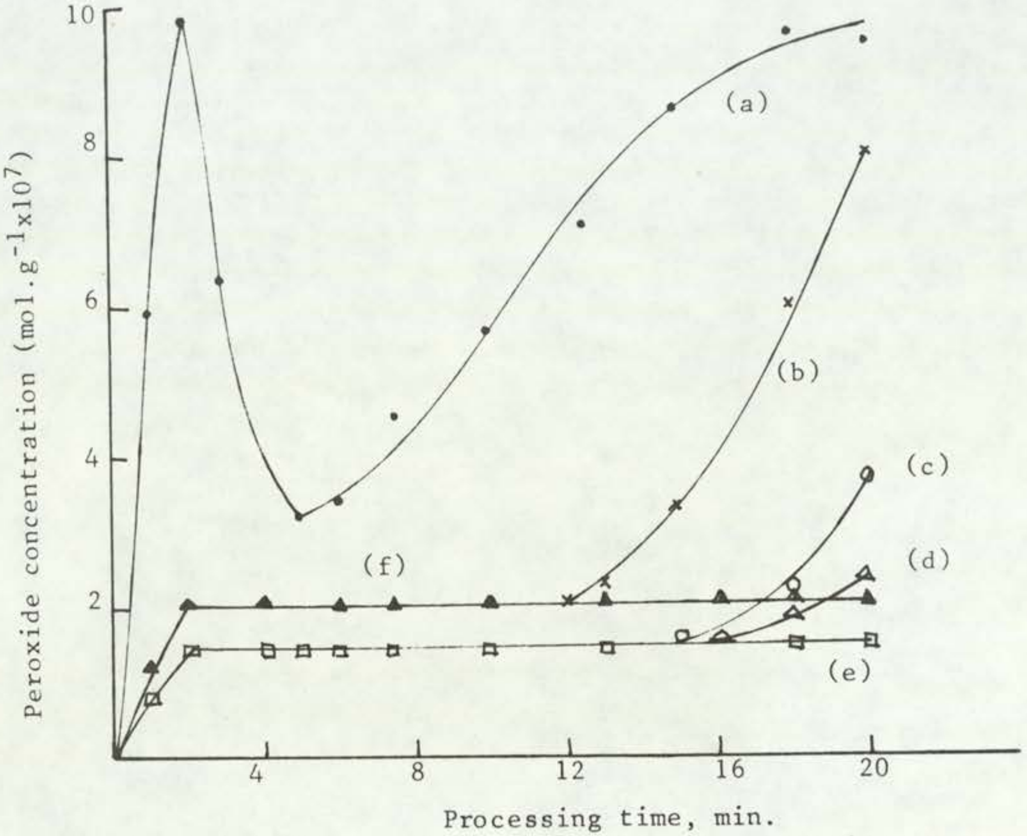


Fig. 4.25: Effect of processing time on peroxide concentration in PVC (a) Control; (b) 5.8x 10^{-3}M DBTM; (c) DBTM + Irg.1300 (d) DBTM + Irg.1076; (e) DBTM + Irg.1010; (5.8:1.4)x10^{-3} mole% (f) 7.2x 10^{-3} mole %DBTM. b-f with lubricants

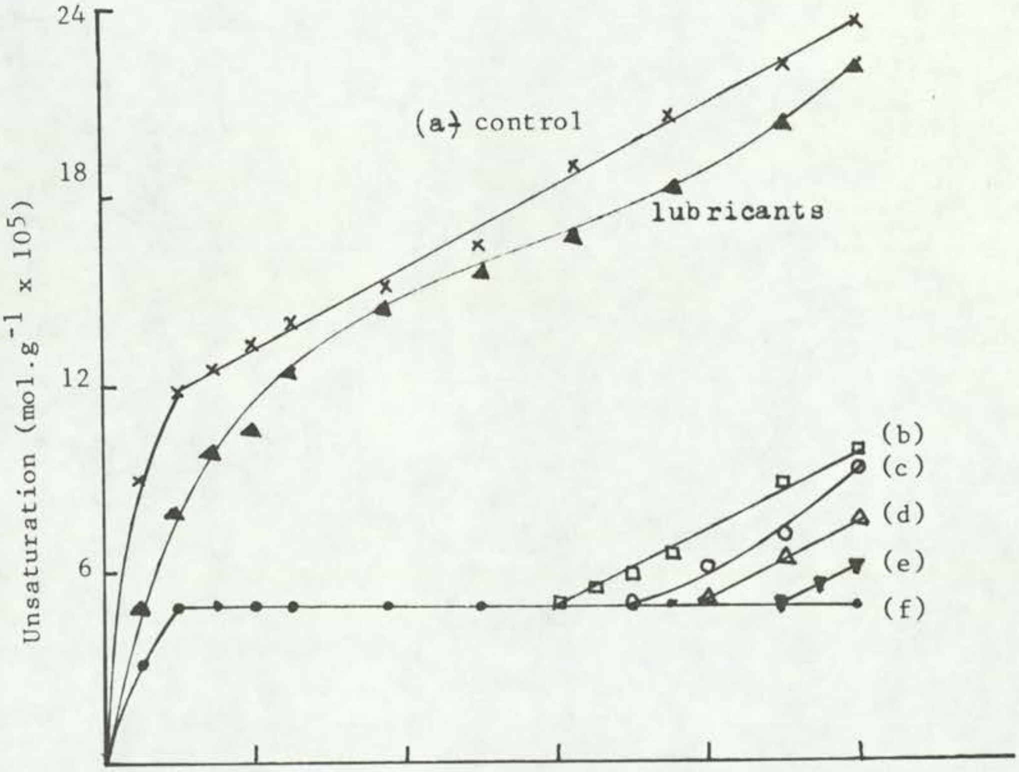


Fig. 4.26: Effect of phenolic antioxidants and DBTM on unsaturation in PVC during thermal processing at 180°C. Captions (b-f) as in fig. 4.25.

have been conducted in the present work (Chapter three) which confirm the earlier findings.[27,18] A systematic investigation of samples formulated with PbSt shows that a similar mechanism is involved in the stabilisation of PVC as in samples stabilised with DBTM. Figure 4.27 shows the decay of the stabiliser's carboxylate i.r. absorbance (1570-1580 cm^{-1}) in PVC stabilised with $5.7x10^{-3}$ mole % of DBTM and PbSt. It is found that the carboxylate group of PbSt decays faster than that of DBTM. The decrease in the carboxylate concentration was paralled by an increase in ester carbonyl ($1735cm^{-1}$) shown in fig. 4.28. Figure 4.29 shows the formation of carbonyl at $1775cm^{-1}$and the associated peak at $1845cm^{-1}$due to maleic anhydride of DBTM and at $1710\text{-}15cm^{-1}$due to stearic acid of PbSt. The formation of maleic anhydride was confirmed by conversion of these species into free acid by boiling with distilled water[27];this method was also adopted in this study (chapter 3). The rapid formation of free acids in samples containing PbSt may well be responsible for the more effective lubricating property of PbSt (see fig. 4.2) since the lubricating characteristics of free saturated acids is a well known phenomenon.[137] Although the ester concentration formed in PVC increased more rapidly in the presence of PbSt than DBTM during the early stages of processing, the optimum concentration of ester formed is higher in the latter formulations. Moreover, the ester group in PbSt reaches a peak and commences to decay earlier than in DBTM (fig. 28).

4.2.3 **Discussion**

The inability of phenolic antioxidants Irg.1300, 1076 and 1010 to synergise with DBTM and PbSt may be rationalised in terms of restricted

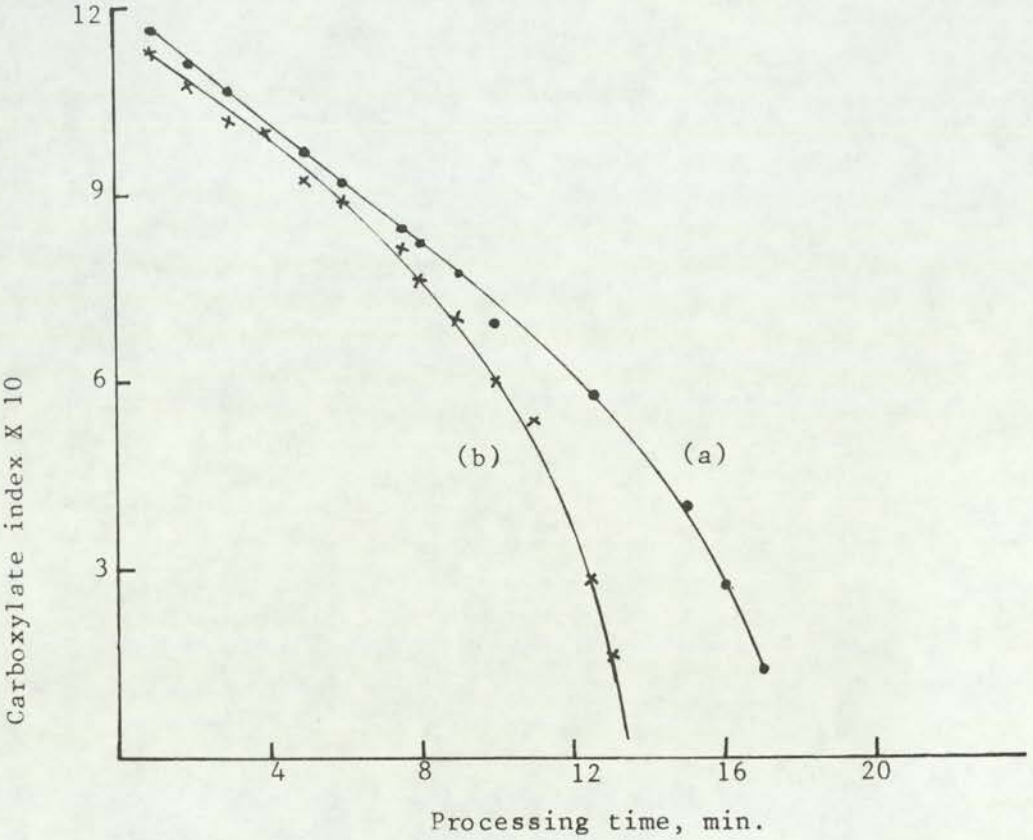


Fig. 4.27: Decay of the stabiliser's cartoxylate i.r. absorbance (1570-1580cm^{-1}) in PVC stabilised with 5.8 x 10^{-3} mole %, (a) DBTM; (b) PbSt.

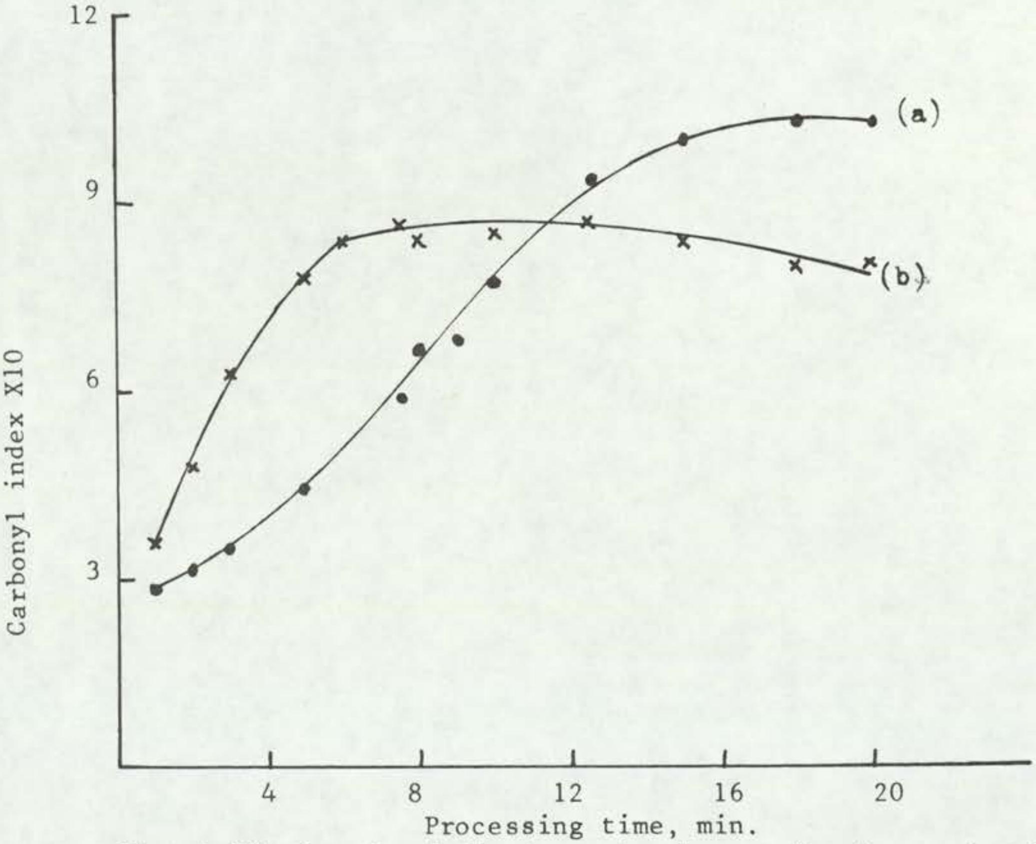


Fig. 4.28: Growth of the i.r. absorbance of ester carbonyl group (1735 cm^{-1}) in PVC stabilised with 5.8x10^{-3} mole %, (a) DBTM; (b) PbSt.

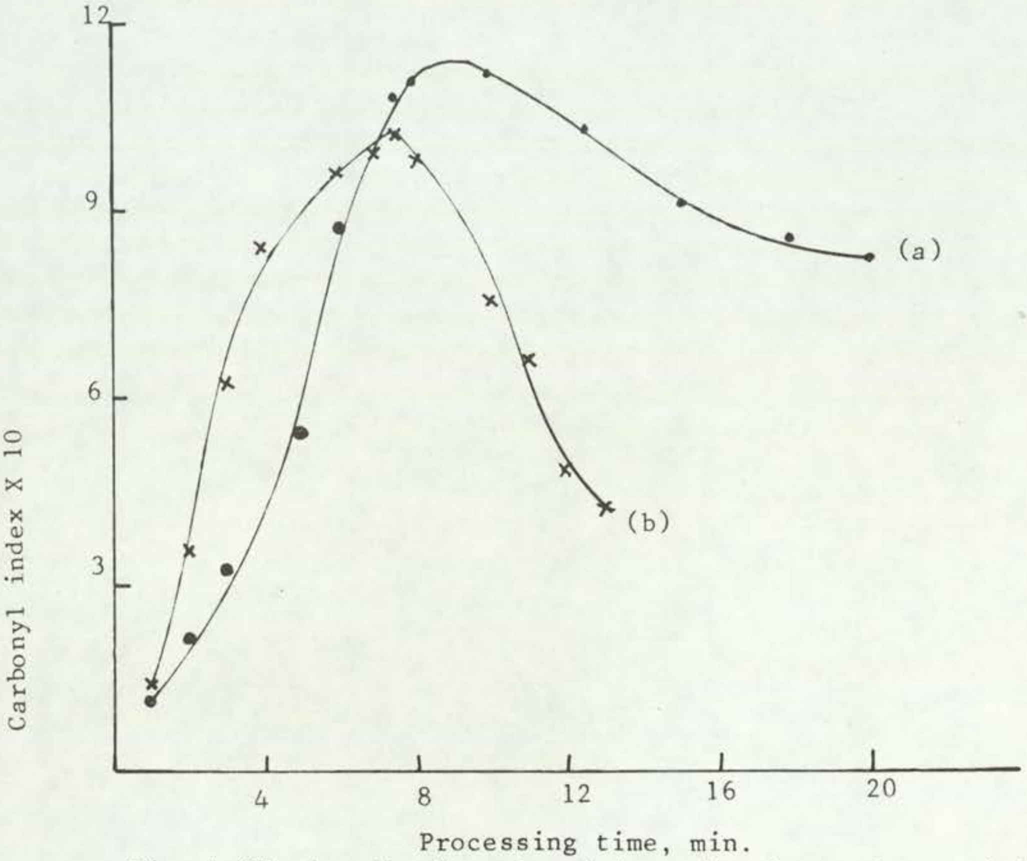


Fig. 4.29: Growth of carbonyl i.r. absorbance from acidic species formed in PVC turning thermal at 180°C (a) 1775cm^{-1}, 5.8x10^{-3} mole %, DBTM; (b) 1715 cm^{-1}; 5.8 x 10^{-3} mole% PbSt.

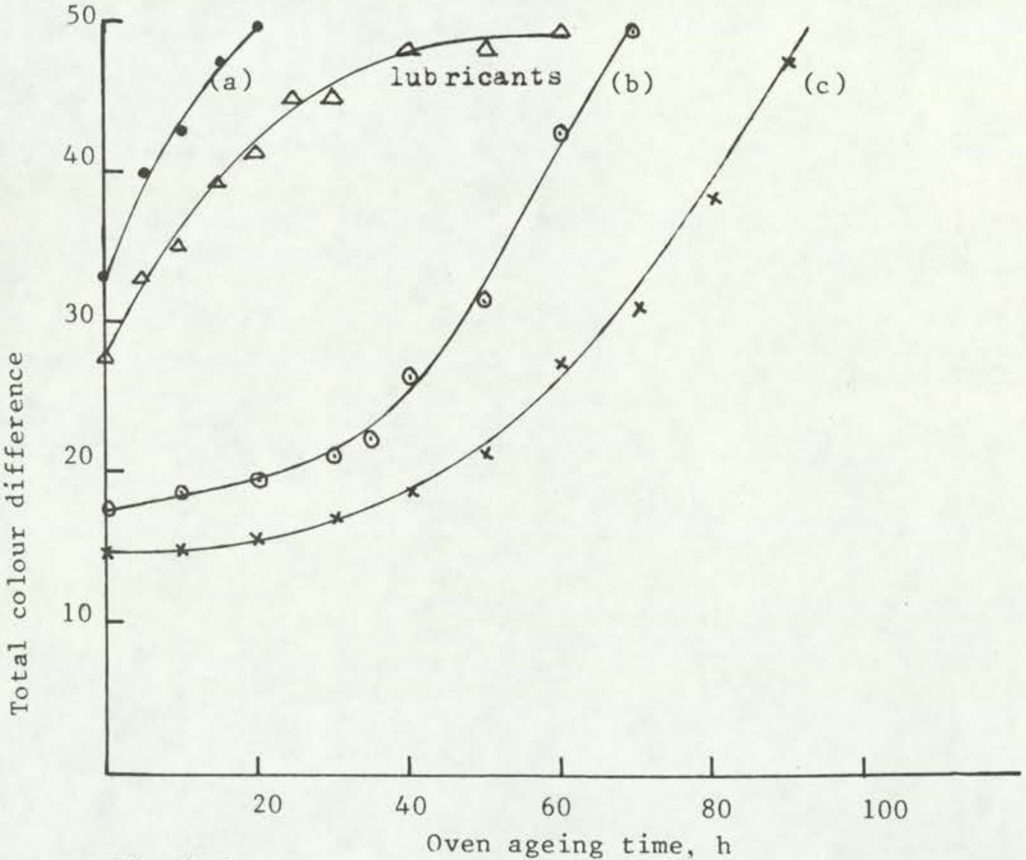
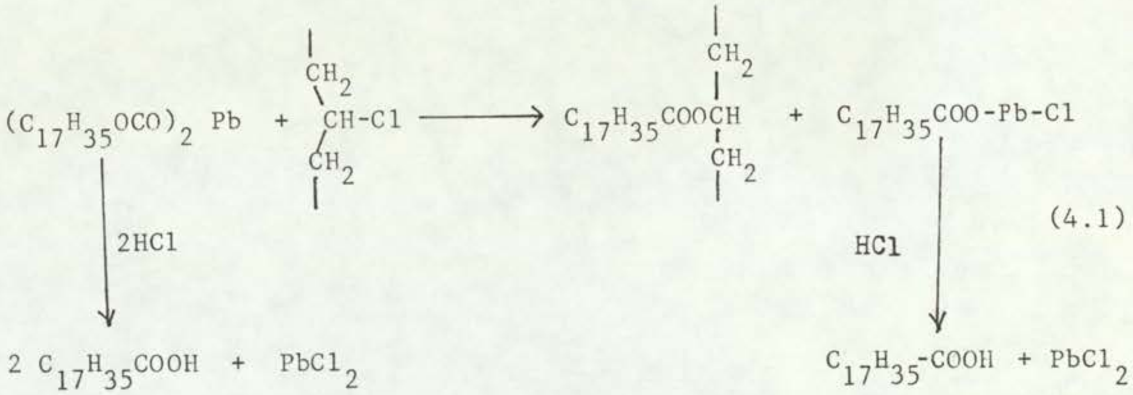


Fig. 4.30: Effect of stabilisers on thermal oxidative colour formation in PVC. (a) Control; (b) PbSt; (c) DBTM, 2.9x10^{-3} mole %.

oxygen availability. During mechanical shear of polymer chains under the processing operation in a closed mixer, the initiation rate is high in terms of chain rupture to give macroalkyl radicals and the only oxygen present is that initially dissolved in the virgin polymer. Under such conditions, alkyl radicals are the major radical propagating species present in the systm and CB-A antioxidants function most effectively. On the other hand, the phenolic antioxidants which are CB-D antioxidants are most effective in an atmosphere of excess oxygen when alkylperoxyl radicals are the predominant species in the autoxidising system. Consequently these CB-D antioxidants are less effective during the processing operation when the concentration of alkylperoxyl radicals which these phenolic antioxidants interrupt is low.

The relative stabilising activities of the phenolic antioxidants was found to be in the order, Irg.1300 1076 1010. At equal molar concentrations at which these antioxidants were used in this work, the superiority of Irg.1010 to both Irg.1300 and 1076 may be explained in terms of multi-functionality since there are four phenolic antioxidant groups per mole of Irg.1010 whereas there is only one phenolic group per mole of both Irg.1300 and 1076. Consequently, the intrinsic antioxidant activity of Irg. 1010 is expected to be greater than both Irg.1300 and 1076. On the basis of functionality both Irg.1300 and 1076 may be expected to give similar stabilising effect as they both contain one phenolic group per molecule. The slight superiority of Irg.1076 over 1300 may be due to the bulkier aliphatic chain in 1076 which most probably increases the compatibility of this antioxidant with PVC over that of Irg. 1300

The replacement of labile chlorine atoms on PVC chains by stable stabiliser's ester groups proposed by Frye and Horst[68] has been used widely to explain the stabilisation of PVC by metal soaps[23,65,69] although other workers[142] have argued that the level of ester incorporated into the polymer chain is rather small. Esterification has also been shown in the stabilisation of PVC by DBTM[53]. The following reactions (4.1) are in agreement with the i.r. spectra discussed above and may well explain the stabilising effect of PbSt in PVC.



(4.1)

4.3 Thermal Oxidative Ageing of PVC

Accelerated thermal oxidative ageing of PVC films was carried out in a Wallace oven at 140°C; each film was aged separately to prevent possible contamination by volatile products from other samples. The degradation of the polymer was monitored by the measurement of functional groups as described in Chapter 2.

Figures 4.30-32 show the total colour difference in PVC in the absence and presence of 2.9, 5.8 and 7.2×10^{-3} mole % respectively of PbSt and

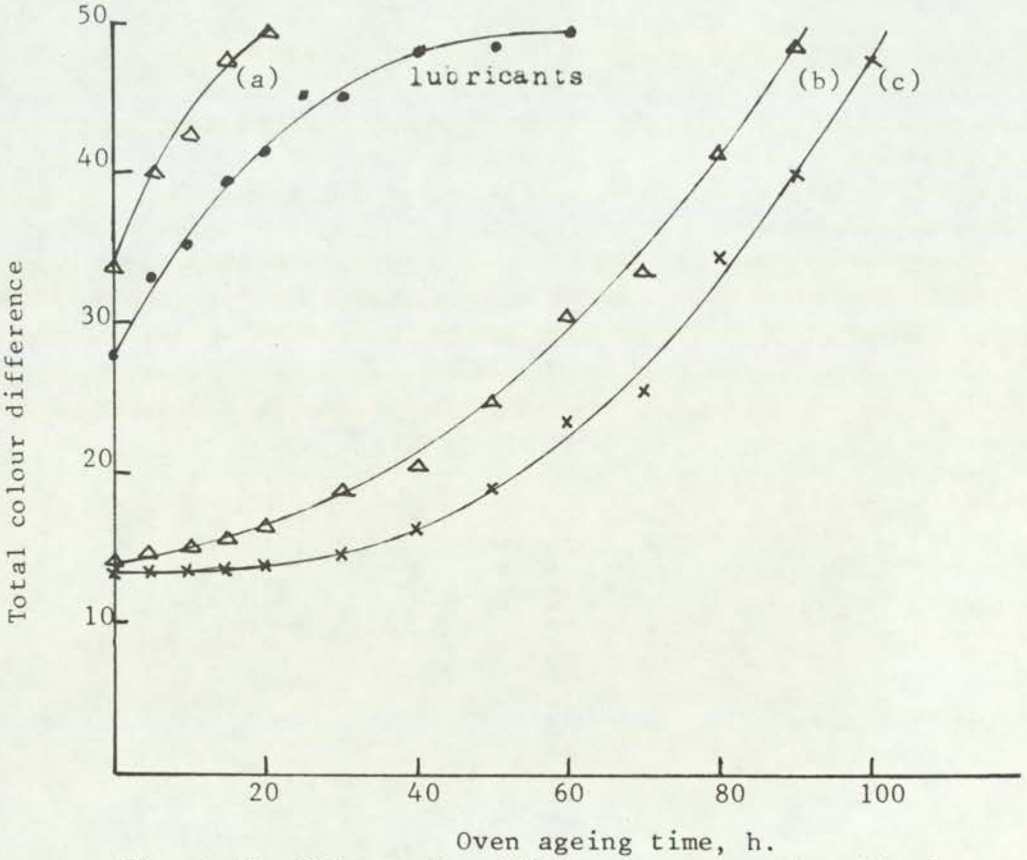


Fig. 4.31: Effect of stabilisers on thermal oxidative colour formation in PVC (a) Control; (b) PbSt; (c) DBTM, 5.8×10^{-3} mole %.

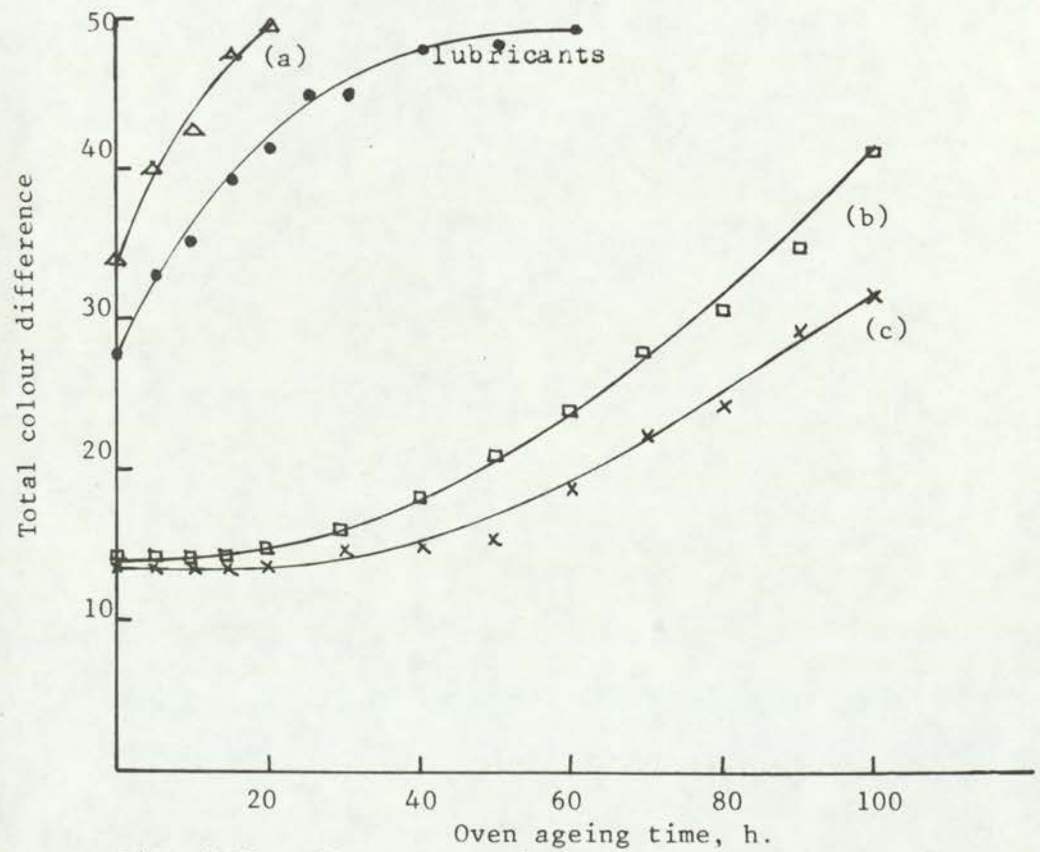


Fig. 4.32: Effect of stabilisers on thermal oxidative colour formation in PVC (a) Control; (b) PbSt; (c) DBTM; 7.2×10^{-3} mole %.

DBTM during oven ageing at 140°C. Both PbSt and DBTM improve the oxidative stability of the polymer but PbSt is less effective than DBTM. The corresponding unsaturation formed in these formulations are shown in figs. 4.33-35. The stabilising activity of both PbSt and DBTM increases with increasing concentration, PbSt being less effective than DBTM at the same molar concentration.

The effect of the more effective stabiliser, DBTM, and its combinations with phenolic antioxidants on the thermal oxidative stability of PVC was investigated in greater detail. Figures 4.36 and 37 compare the thermal oxidative stability of the control sample with samples stabilised with 2.9, 5.8 and 7.2 x 10^{-3} mole % DBTM. The addition of phenolic antioxidants to DBTM formulations gives improved thermal oxidative stability as measured by both total colour difference, figs. 4.38-40, and unsaturation, figs. 4.41-43. At equal molar concentrations the thermal oxidative antioxidant activity of the phenolic antioxidants is found to be in the order Irg.1300 1076 1010 similar to the order of their stabilising effects under thermal processing operation at 180°C. The effect of increasing concentrations of phenolic antioxidants on oven ageing embrittlement time of samples stabilised with $5.8\text{x}10^{-3}$ mole% DBTM is shown in fig. 4.44. The additional thermal oxidative stability of the DBTM/Irganox mixtures increases with increasing concentration of the three phenolic antioxidants although in the case of Irg.1010 the increase in stability beyond 1.2 $\text{x}10^{-3}$ mole % is rather small. This levelling up of the oxidative stability in the presence of higher concentrations of Irg.1010 is not as obvious in the case of Irg.1076 and this phenomenon seems absent altogether in the case of Irg.1300 at least up to $2\text{x}10^{-3}$ mole %.

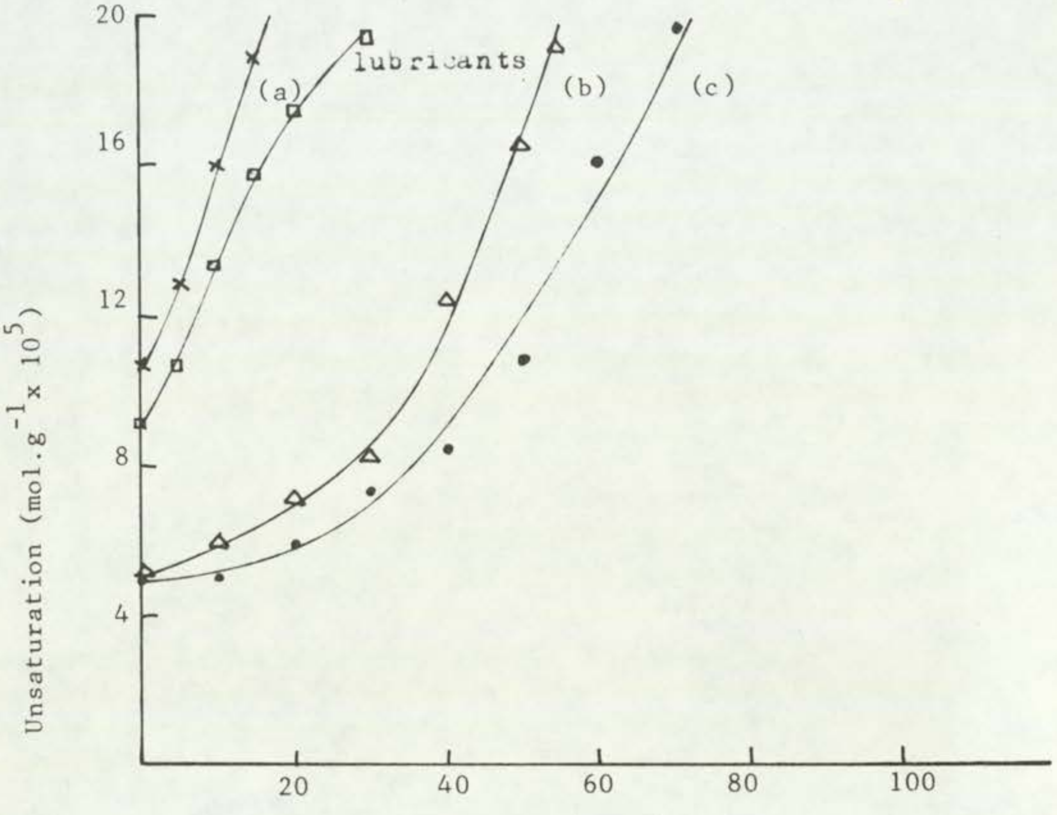
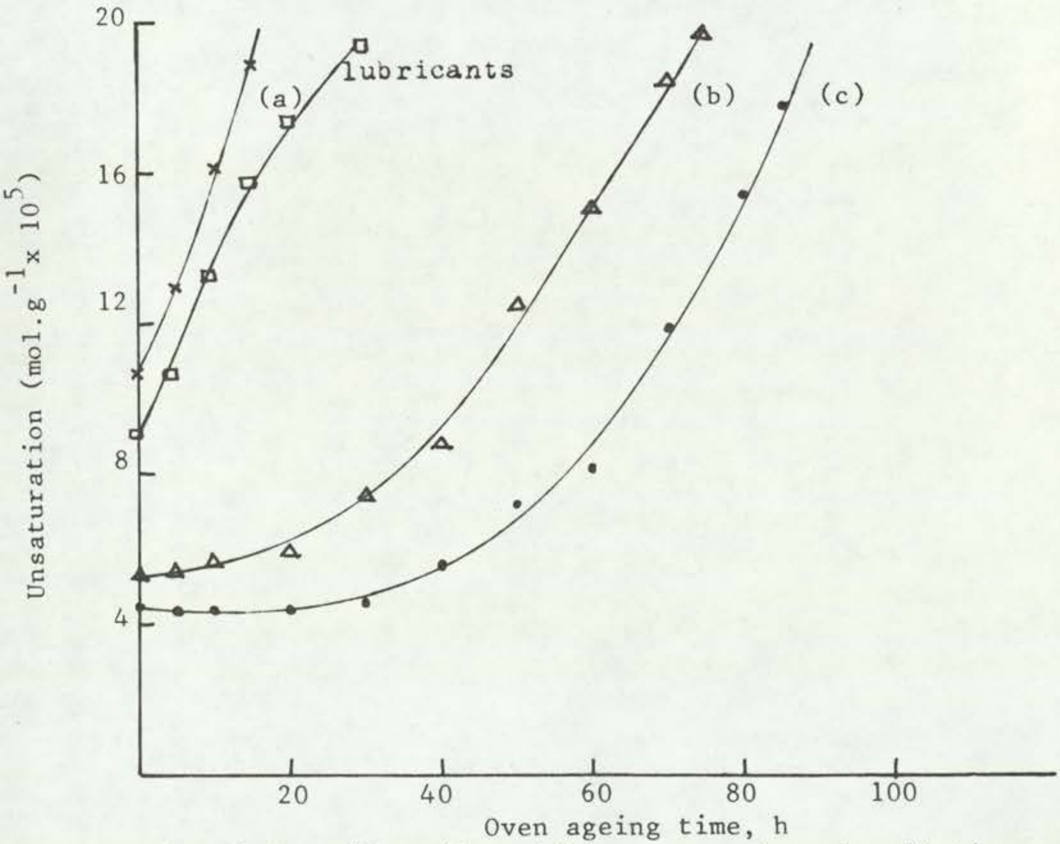


Fig. 4.33 Oven ageing time, h.
Effect of stabilisers on thermal oxidative unsaturation formation in PVC. (a) Control; (b) PbSt; (c) DBTM, 2.9 x 10^{-3} mole %



Oven ageing time, h
Fig. 4.34: Effect if stabilisers on thermal oxidative unsaturation formation in PVC. (a) Control; (b) 5.8x10^{-3} mole % DBTM; (c) 5.8x10^{-3} mole % DBTM.

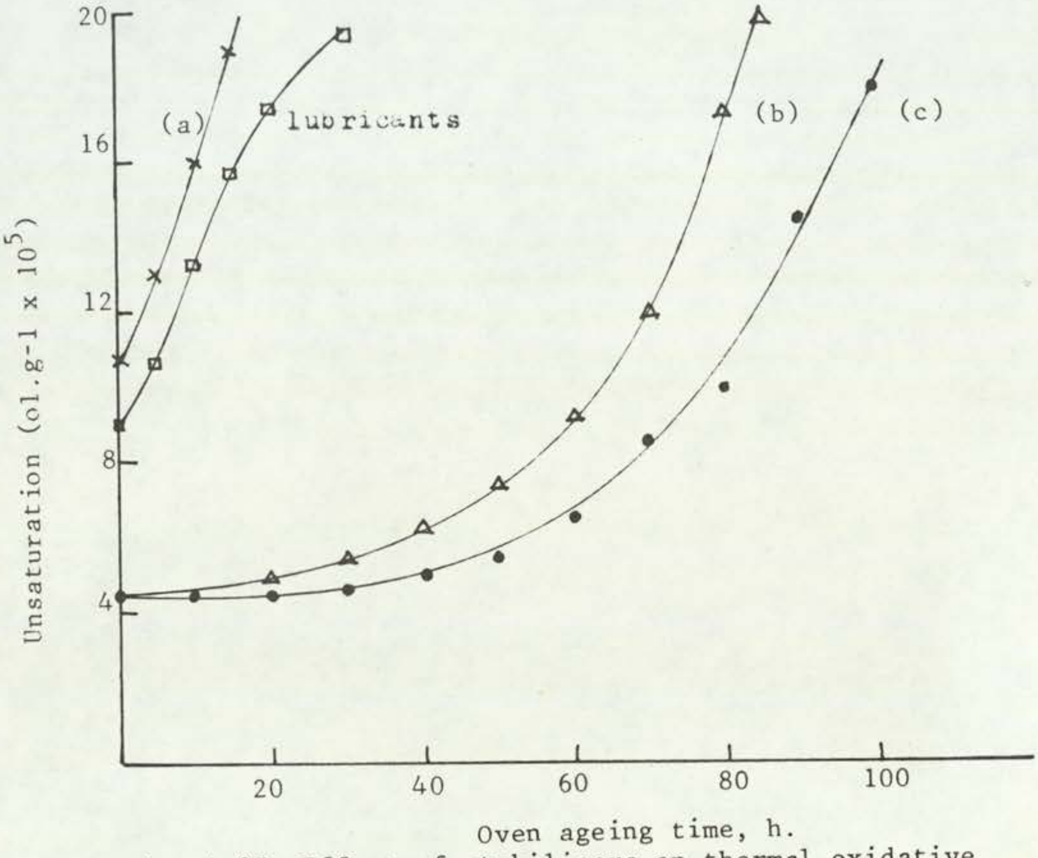


Fig. 4.35: Effect of stabilisers on thermal oxidative unsaturation formation in PVC. (a) Control; (b) 7.2 x10^{-3}M PbSt; (c) 7.2x10^{-3}M DBTM.

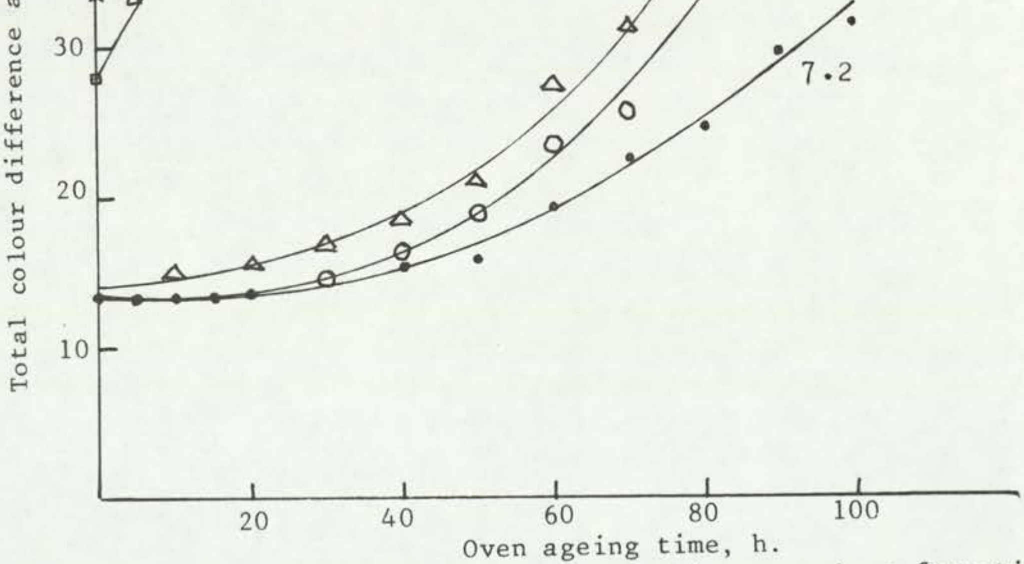


Fig. 4.36: Effect of DBTM concentration on colour formation in PVC. Numbers on the curves represent concentration of DBTM in 10^{-3}M.

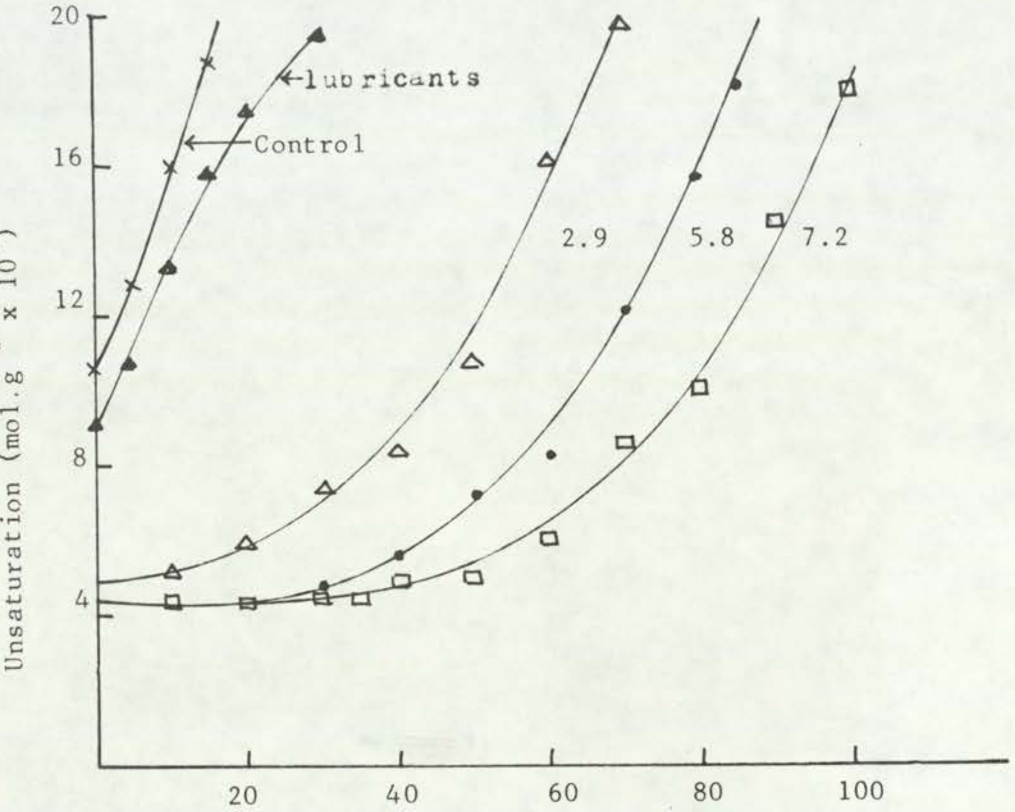


Fig. 4.37: Effect of DBTM concentration on unsaturation in PVC during oven ageing (140°C), Numbers on the curves represent concentration of DBTM in 10^{-3}M.

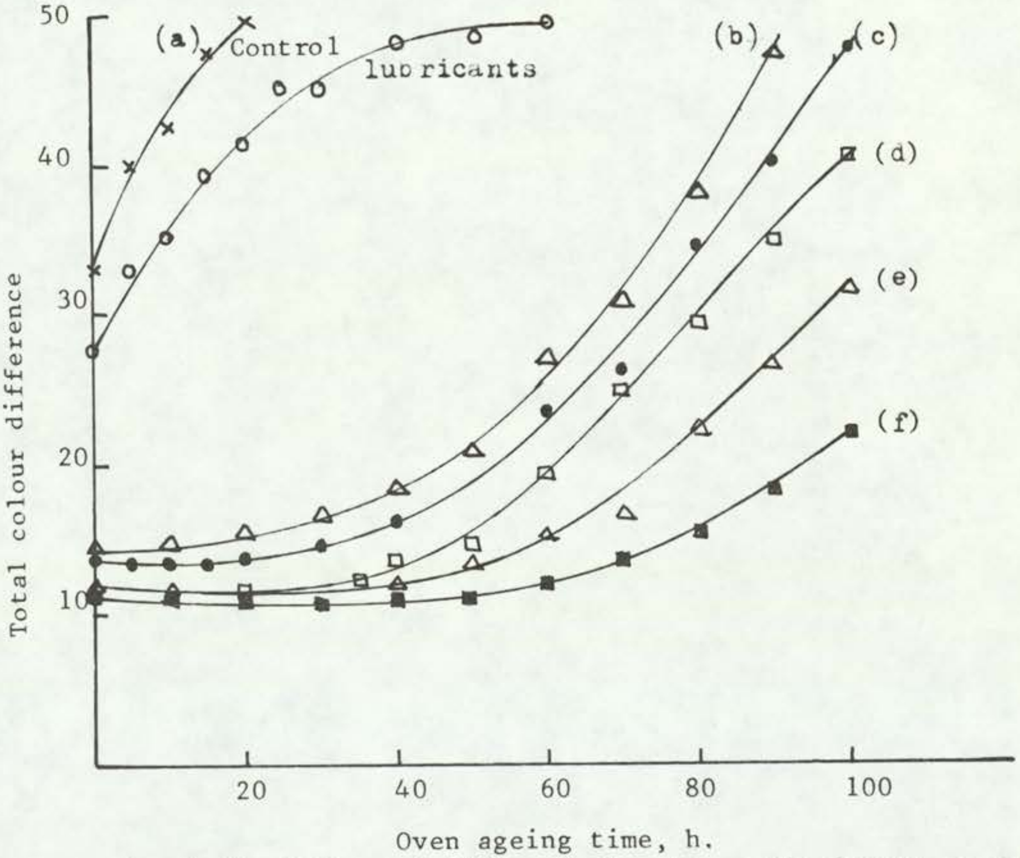


Fig. 4.38: Effect of DBTM and phenolic antioxidants on colour formation in PVC during oven ageing at 140°C. (a) Control; (b) 2.9×10^{-3}M DBTM; (c) 5.8×10^{-3}M DBTM (d) DBTM/Irg.1300; (e) DBTM/Irg.1076· (f) DBTM/Irg.1010 (c-f: $2.9/2.9\times10^{-3}$)

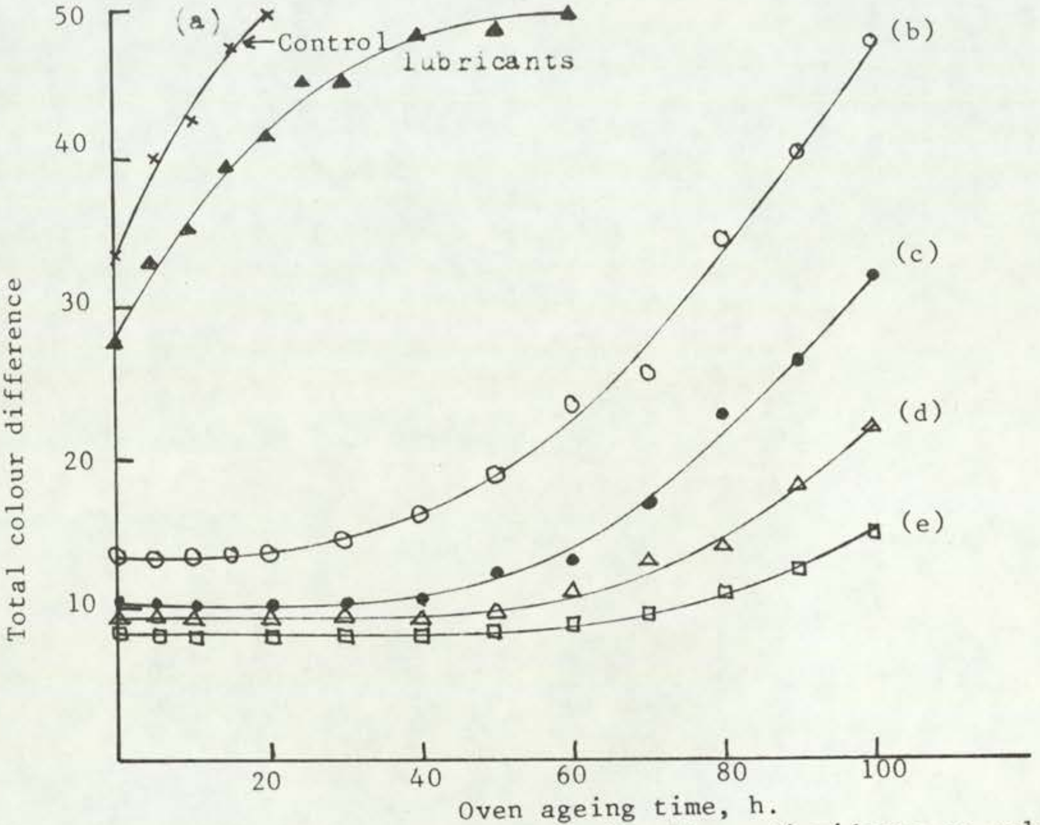


Fig.4.39: Effect of DBTM and phenolic antioxidants on colour formation in PVC during oven ageing at 140°C. (a) Control; (b)5.8×10^{-3}M DBTM; (c)DBTM/Irg.1300; (d) DBTM/Irg.1076; (e) DBTM/Irg.1010 (c-e:$4.3/1.5\times10^{-3}$M.

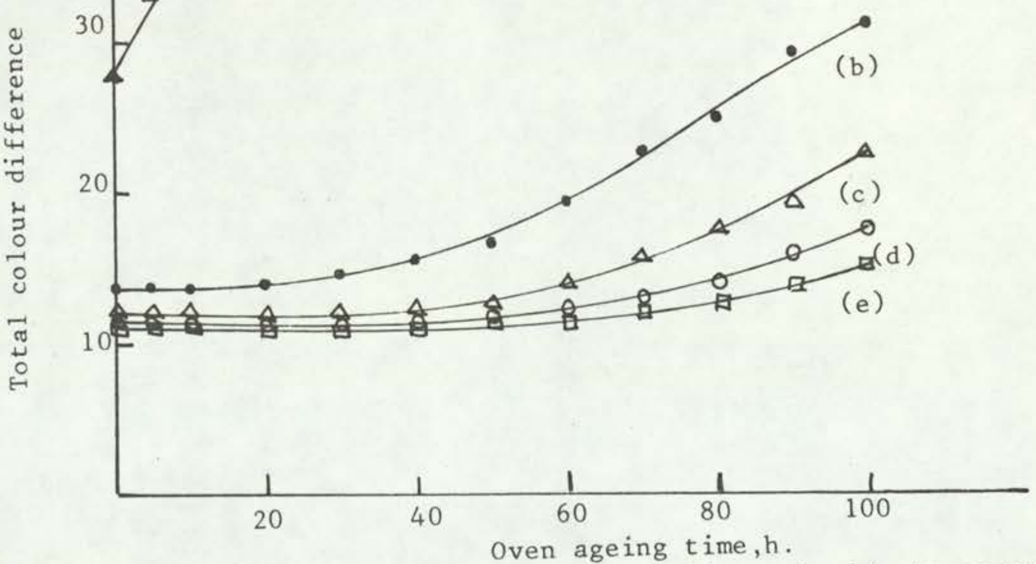


Fig. 4.40: Effect of DBTM and phenolic antioxidants on colour formation in PVC during oven ageing at 140°C. (a) control; (b)7.2×10^{-3}M DBTM; (c) DBTM/Irg.1300; (d)DBTM/Irg.1076; (e) DBTM/Irg.1010 (c-e;$5.8/1.4\times10^{-3}$M).

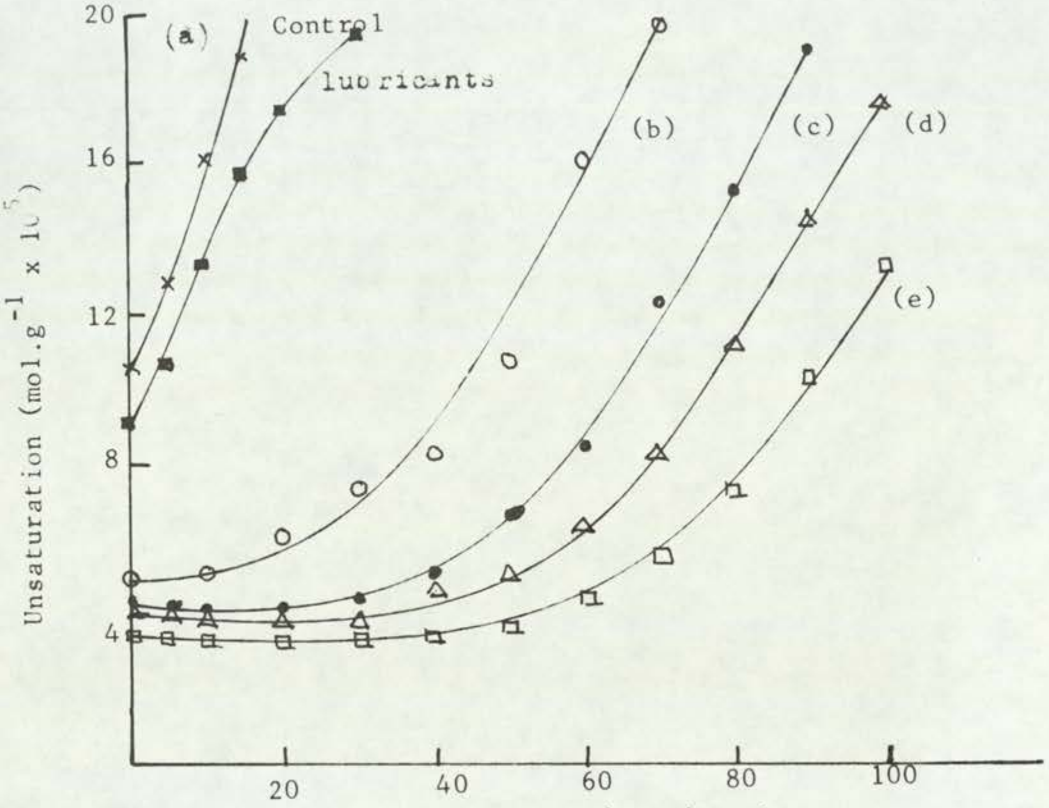


Fig. 4.41: Effect of DBTM and phenolic antioxidants on unsaturation in PVC during oven ageing at 140°C. (a) Control; (b) 2.9×10^{-3}M DBTM; (c) DBTM/Irg.1300; (d) DBTM/Irg.1076; (e) DBTM/Irg.1010, (c-e: $2.9/2.9 \times 10^{-3}$M).

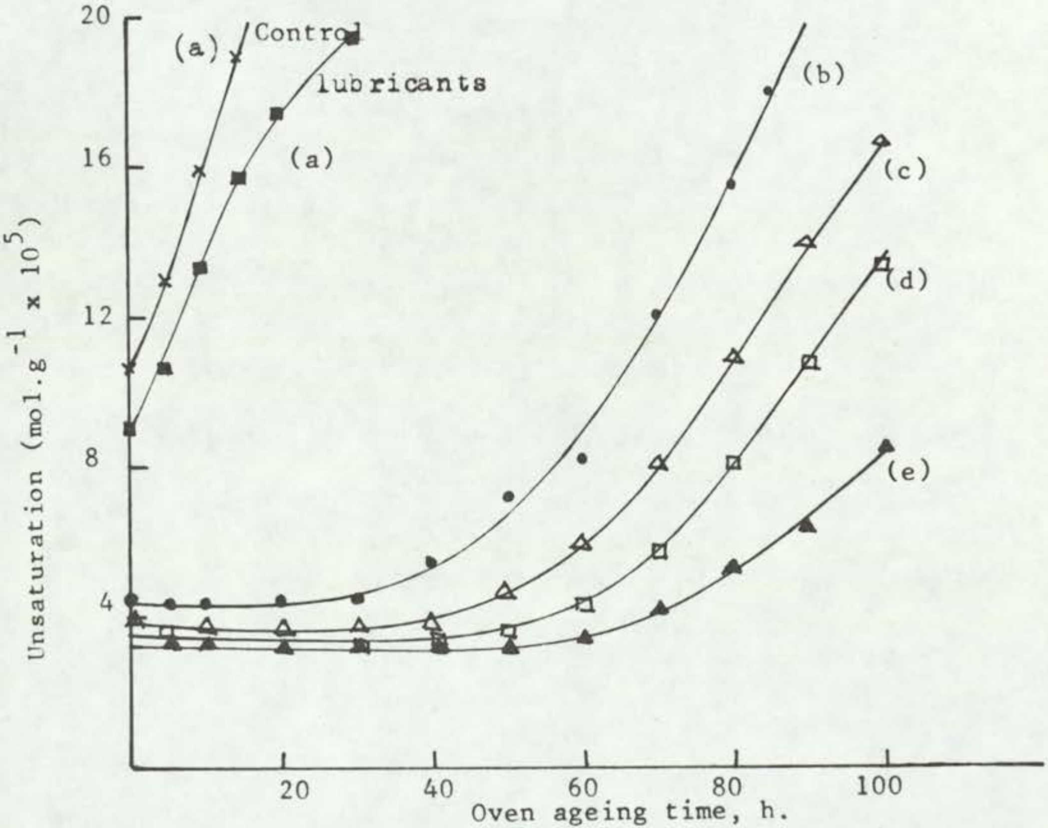


Fig. 4.42: Effect of DBTM and phenolic antioxidants on unsaturation in PVC during oven ageing at 140°C. (a) Control; (b)5.8×10^{-3}M DBTM; (c)DBTM/Irg.1300; (d)DBTM/Irg.1076; (e)DBTM/Irg.1010. (c-e: $4.3/1.5 \times 10^{-3}$ M).

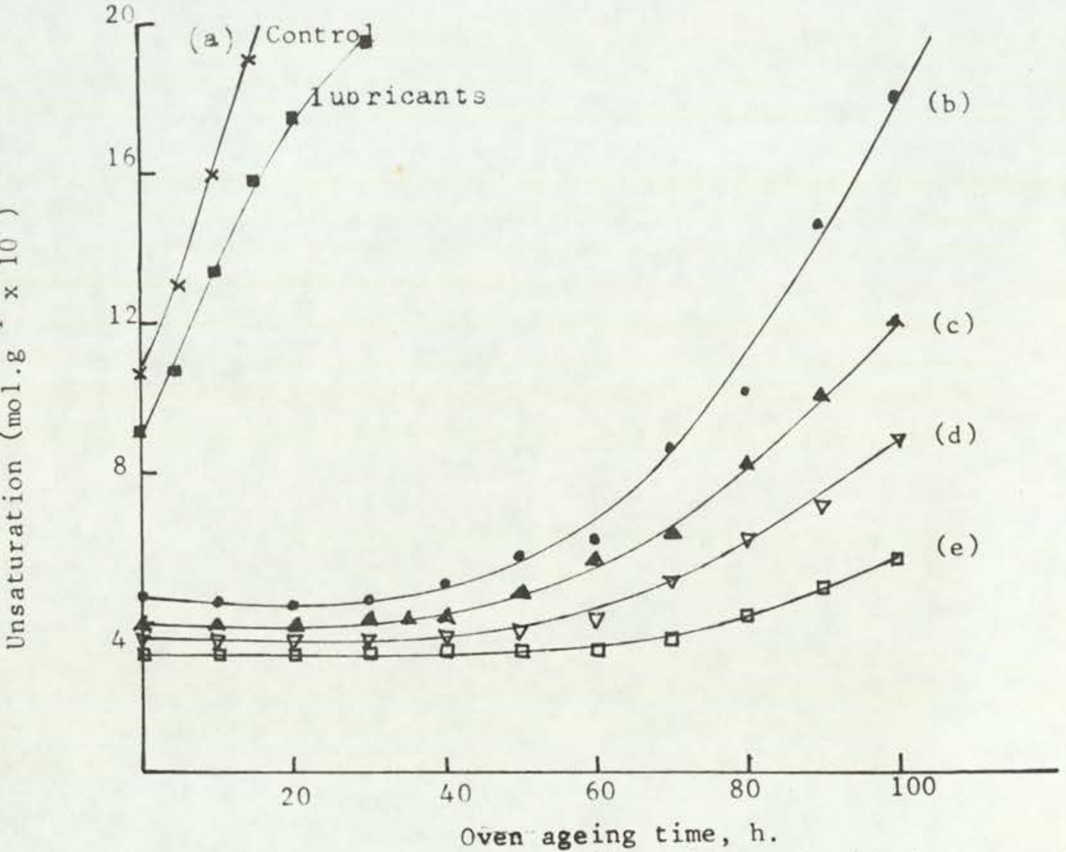


Fig.4.43: Effect of DBTM and phenolic antioxidants on unsaturation in PVC during oven ageing at 140°C (a) Control; (b) 7.2×10^{-3}M DBTM; (c) DBTM/Irg.1300; (d) DBTM/Irg.1076; (e) DBTM/Irg.1010 (c-e: $5.8/1.4 \times 10^{-3}$ M).

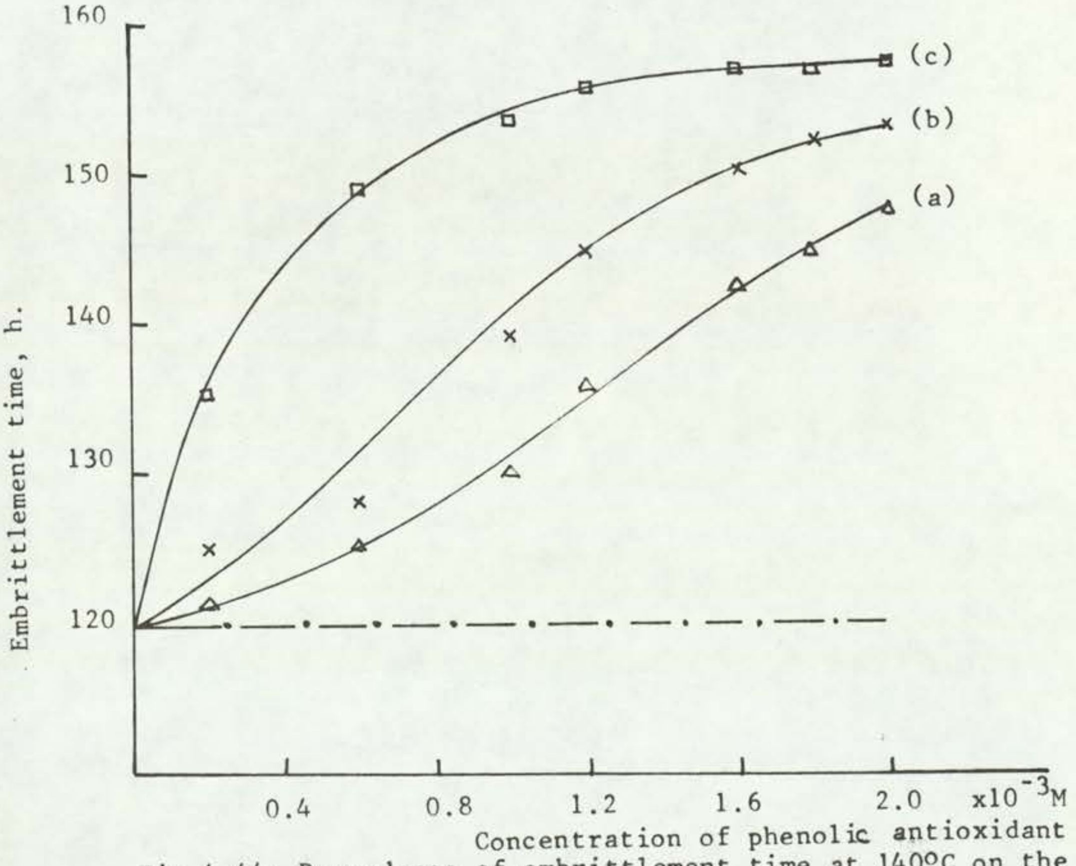


Fig.4.44: Dependence of embrittlement time at 140°C on the concentration of phenolic antioxidant in combination with 5.8×10^{-3}M DBTM (-.-).(a)Irg.1300;(b)Irg1076; (c) Irg. 1010.

4.3.1 Discussion

Scott and co-workers[143-145] showed that under oven ageing conditions (140^oC), the loss of phenolic antioxidants by volatilisation was much more important than the intrinsic activity of the antioxidants in a closed system. As such, antioxidants with high molecular weight and low volatility are important in oven ageing test. The present results discussed above lend further support to the earlier reports[143-145] since the effectiveness of the antioxidant activity was found to be in the same order of their molecular weights: Irg.1300 1076 1010 (figs.4.38-43). The molecular weights of these antioxidants are 292, 530 and 1176 respectively. Detailed investigations[146] of a homologous series of phenolic thiol antioxidants also showed similar trends in which antioxidant activity increases with increasing molecular weight and decreasing volatility. The superior antioxidant activity of Irg.1010 than both Irg. 1300 and 1076 in the present work may not be completely attributed to the higher molecular weight and lower volatility of Irg.1010 but may be due in part ot its multi (tetra)-phenolic antioxidant functions per mole as against only one phenolic antioxidant function for both Irg.1300 and 1076.

It has been shown earlier (section 4.22) that all the three phenolic CB-D antioxidants are less effective than both DBTM and PbSt during processing neither do they show synergism under this condition whereas they are synergistic during thermal oxidation. The effectiveness of phenolic CB-D antioxidants under oven ageing conditions may be explained on the basis of the radical chain autoxidation mechanism originally proposed by Bolland[87] and Bateman[88,89].

$$\begin{aligned} R^{\cdot} + O_2 &\xrightarrow{(a)} ROO^{\cdot} \\ ROO^{\cdot} + RH &\xrightarrow{(b)} ROOH + R^{\cdot} \qquad (4.2) \end{aligned}$$

For most polymers, the second step (eq. 4.2b) is rate-determining and hence, at normal oxygen pressures, the radical present in highest concentration in the autoxidising system is alkylperoxyl, $ROO^{\cdot}$[89]. A practical consequence of this is that termination normally occurs predominantly by reaction of this species (4.3a). Under such conditions,

$$\begin{aligned} 2\,ROO^{\cdot} &\xrightarrow{(a)} \text{disproportionation products} \\ ROO^{\cdot} + R^{\cdot} &\xrightarrow{(b)} ROOR \qquad (4.3) \\ 2R^{\cdot} &\xrightarrow{(c)} R - R \end{aligned}$$

CB-D antioxidants function most effectively[75] and this explains the synergism obtained between Irg. 1300,1076 and 1010 and DBTM (figs. 4.38-43).

There are however, some exceptions to the above generalisation of practical importance (4.3a). The first is when oxygen is deficient in the system[89] as in the barrel of a screw extruder. The second is when the rate of initiation is high compared with the rate of diffusion of oxygen into the polymer, for example during u.v. initiated oxidation[44] or in mechanically induced oxidation during polymer processing or during flexing of rubbers in service. In all cases, the alkyl radical concentration will be higher than in normal thermal oxidation and the termination steps (4.3b, c) assume greater importance. Under such conditions, CB-A antioxidants function most effectively whereas the complementary CB-D antioxidants are much less effective under the same conditions.[75] In agreement with this prediction, the phenolic CB-D antioxidants Irg.1300, 1076 and 1010 were found to be less effective during thermal processing in a closed mixer (Section 4.22).

4.4 Photo-oxidative Ageing of PVC

Photo-oxidative ageing of PVC films was carried out in a u.v. cabinet and the degradation was monitored by total colour difference and embrittlement. Experimental details were outlined in chapter 2.

Table 4.1 shows the embrittlement times obtained during u.v. exposure of PVC samples stabilised with 2.9, 5.8 and 7.2 x 10^{-3} mole % DBTM and PbSt.

Table 4.1 UV Embrittlement Time (h) of PVC stabilised with DBTM and PbSt

Processing Time (min)	Additive concentration x 10^{-3}M	DBTM	PbSt	Control
5	2.9	802	774	658
10	2.9	768	732	600
15	2.9	725	680	587
20	2.9	677	642	562
5	5.8	950	896	-
10	5.8	920	864	-
15	5.8	870	818	-
20	5.8	844	770	-
5	7.2	972	898	-
10	7.2	972	898	-
15	7.2	925	865	-
20	7.2	925	850	-

It is seen from the data that the photo-oxidative stability of both unstabilised and stabilised samples decreases with increasing processing time. The control sample (unstabilised) embrittles much earlier than the stabilised samples. The photo-oxidative stability of both samples containing DBTM and PbSt increases with increasing concentration of the stabiliser, however, at equal concentrations, formulations containing DBTM are found to be superior to those of PbSt.

The effect of u.v. irradiation on unsaturation and total colour difference in the absence and presence of 7.2 $x10^{-3}$ mole % DBTM and PbSt are shown in figs. 4.45 and 46 respectively. Lubricants which reduced the shearing forces operating on the polymer chains during the processing operation improve the photo-oxidative stability of PVC to some extent (curve b of figs. 4.45 and 46). Both unsaturation and total colour difference are reduced by DBTM and PbSt although PbSt is again less effective than DBTM. Figures 4.47 and 48 show the effect of DBTM/Irg 1300 mixture on photo-oxidative accumulation of unsaturation and total colour respectively. It is found that DBTM/Irg 1300 (2.9/2.9 $x10^{-3}$ mole %) mixture improves the stability of PVC only slightly indicating that the mixture functions as a weak photostabilising system for PVC.

The effect of DBTM/Irg.1076 on unsaturation and total colour difference during uv exposure is shown in figs. 4.49 and 50 respectively. Similar effects of DBTM/Irg.1010 are shown in figs. 4.51 and 52. For the purpose of comparison, the effects of the three mixtures on unsaturation and total colour are shown in figs. 4.53 and 54 respectively. Similar to

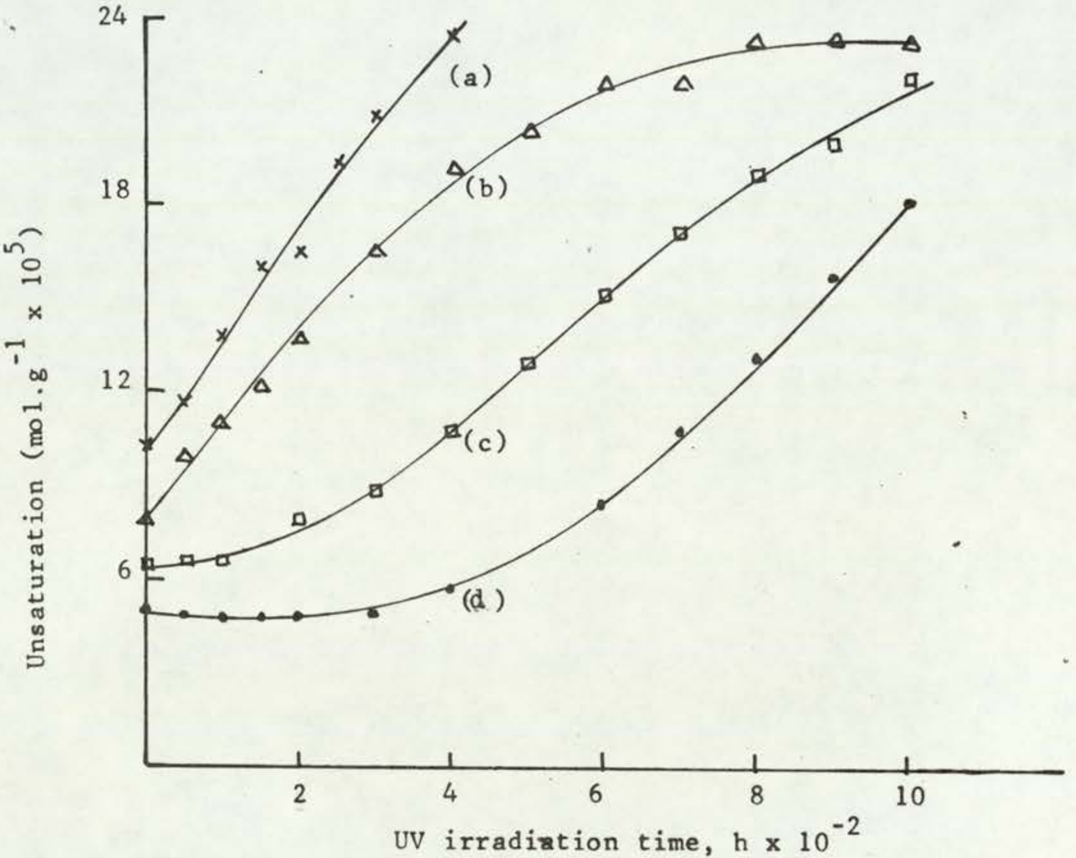


Fig. 4.45: Effect of uv irradiation on unsaturation in PVC processed for 6min. at 180°C. (a) Control; (b) Lubricants; (c) 7.2×10^{-3}M PbSt; (d) 7.2×10^{-3}M DBTM.

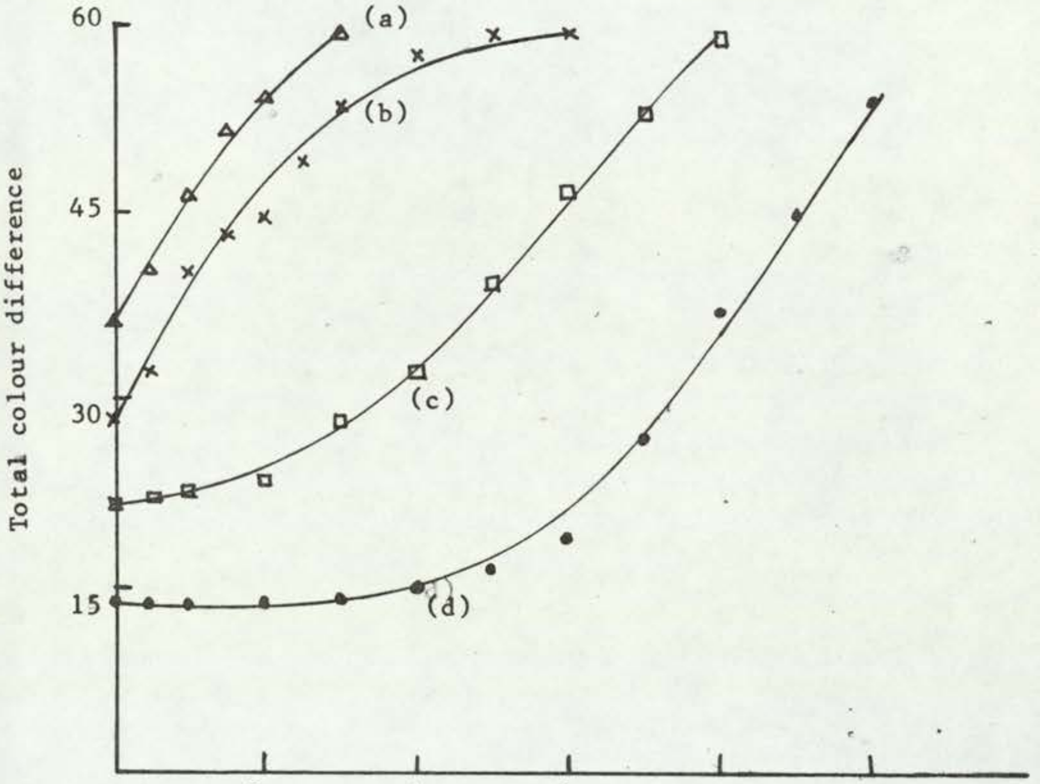


Fig. 4.46: Effect of uv i-radiation on colour formation in PVC processed for 6 min. at 180°C. (a-d) as in fig. 4.45.

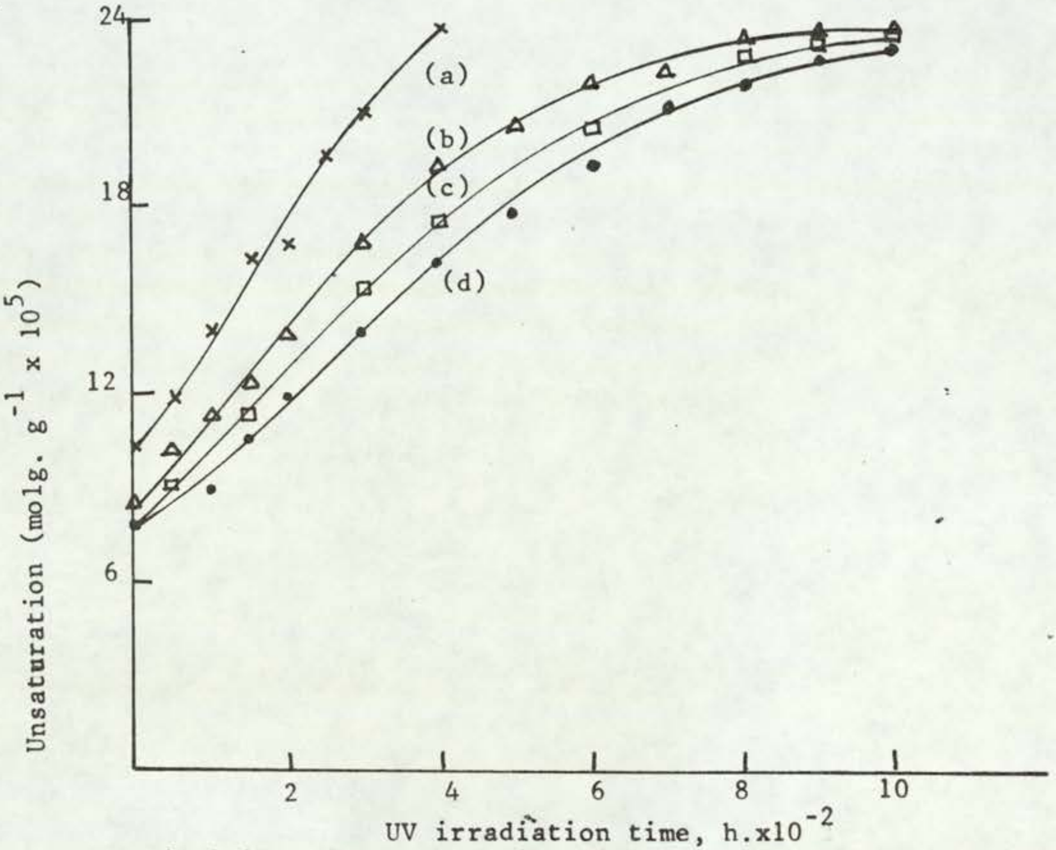


Fig.4.47: Effect of uv irradiation on unsaturation in PVC processed for 6 min. at 180°C. (a) Control; (b) Lubricants; (c) PbSt+Irg.1300 (2.9:2.9): (d) DBTM + Irg.1300 (2.9:2.9) x 10^{-3}M.

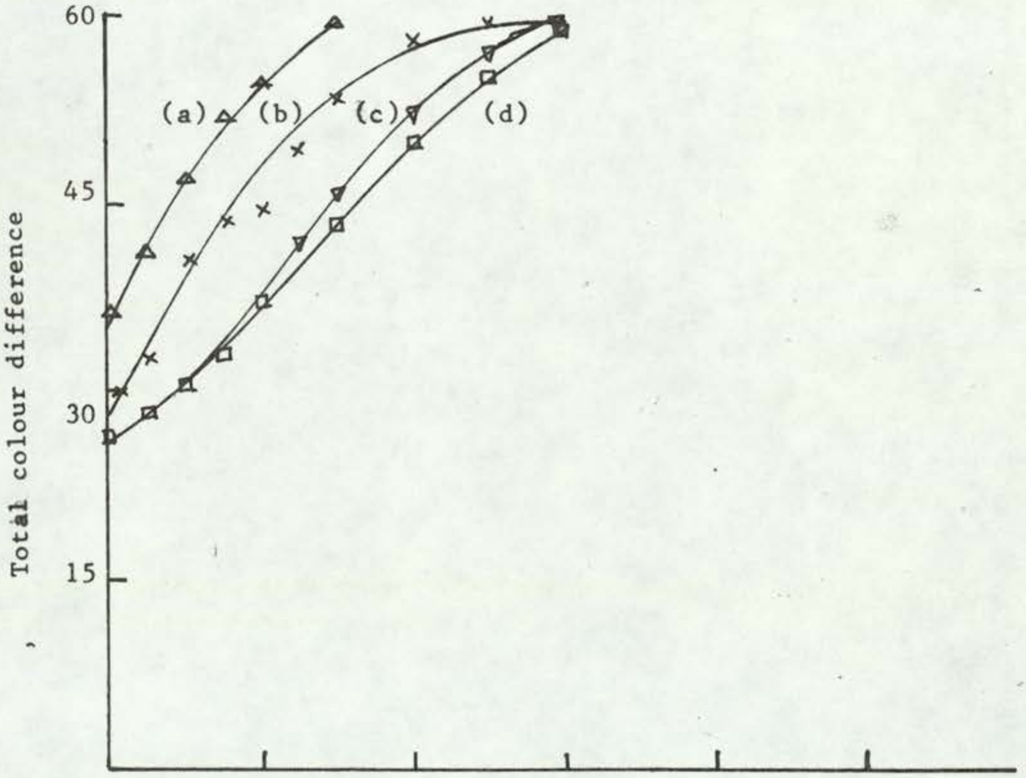


Fig. 4.48: Effect of uv irradiation on colour formation in PVC processed for 6 min. at 180°C (a-d) as in fig. 4.47.

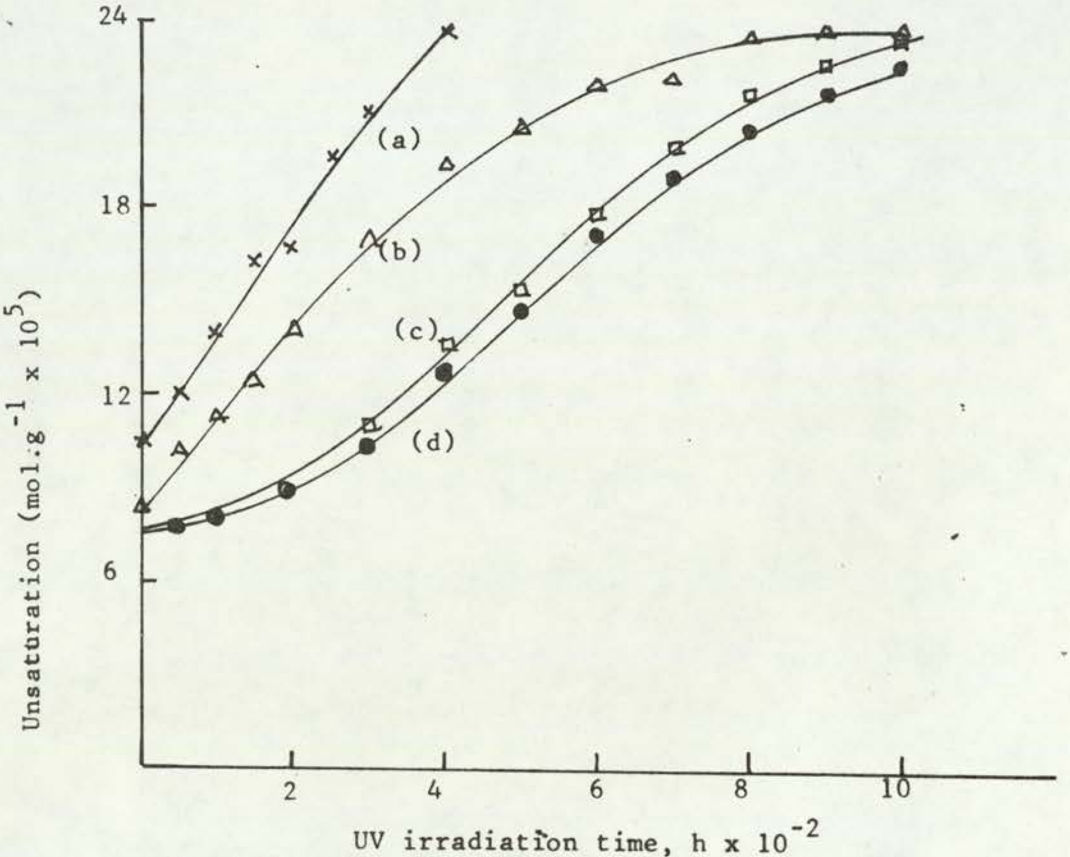


Fig. 4.49: Effect of uv irradiation on unsaturation in PVC processed for 6 min. at 180°C. (a) Control; (b) Lubricants; (c) PbSt + Irg.1076 (2.9:2.9); (d) DBTM + Irg.1076 (2.9:2.9) x 10^{-3} mole % c,d with lubricants.

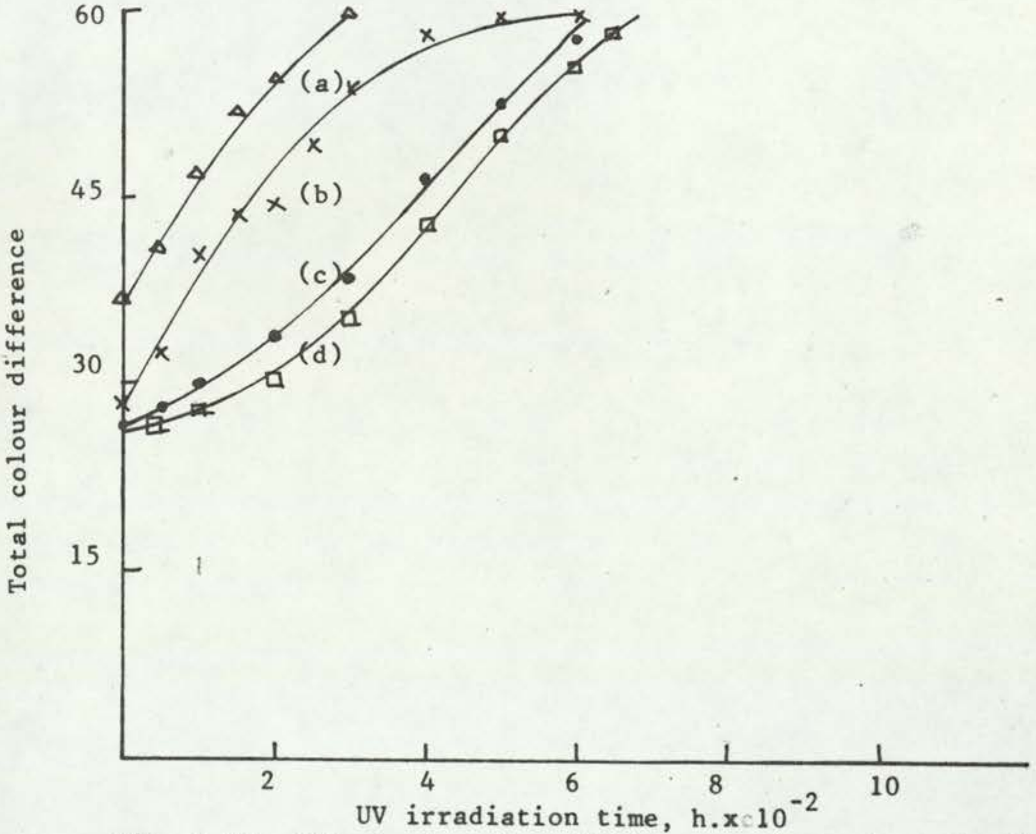


Fig. 4.50: Effect of uv irradiation on colour formation in PVC processed for 6 min. at 180°C. (a-d) as in fig. 4.49)

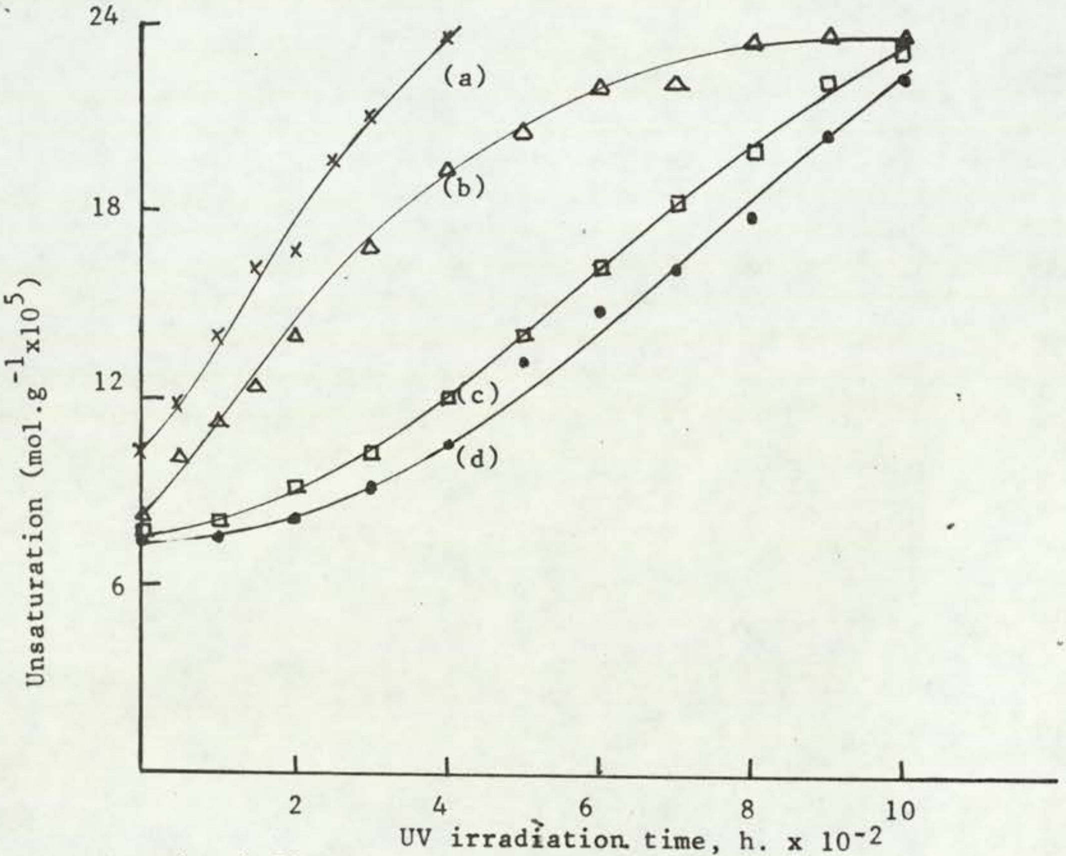


Fig. 4.51: Effect of uv irradiation on unsaturation in PVC processed for 6 min. at 180°C. (a) Control; (b) Lubricants; (c) PbSt+Irg.1010 (2.9:2.9): 9d) DBTM +Irg.1010 (2.9:2.9) x 10^{-3} mole % c,d with lubricants.

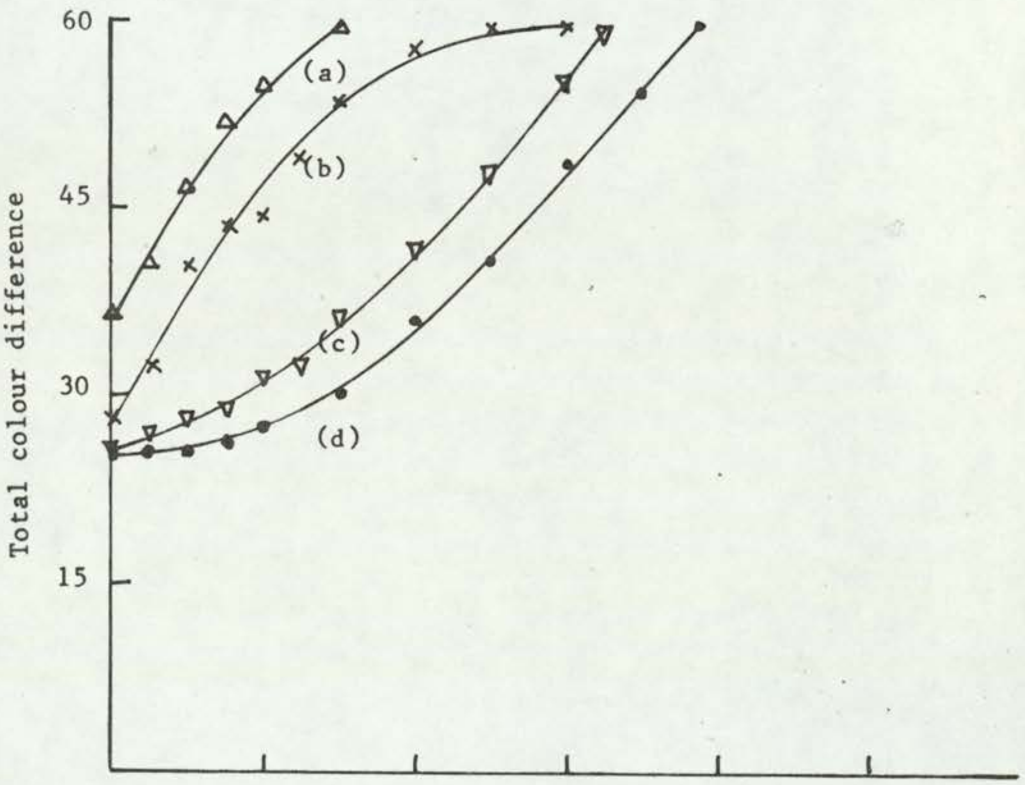


Fig. 4.52: Effect of uv irradiation on colour formation in PVC processed for 6 min. at 180°C (a-d) as in fig. 4.51.

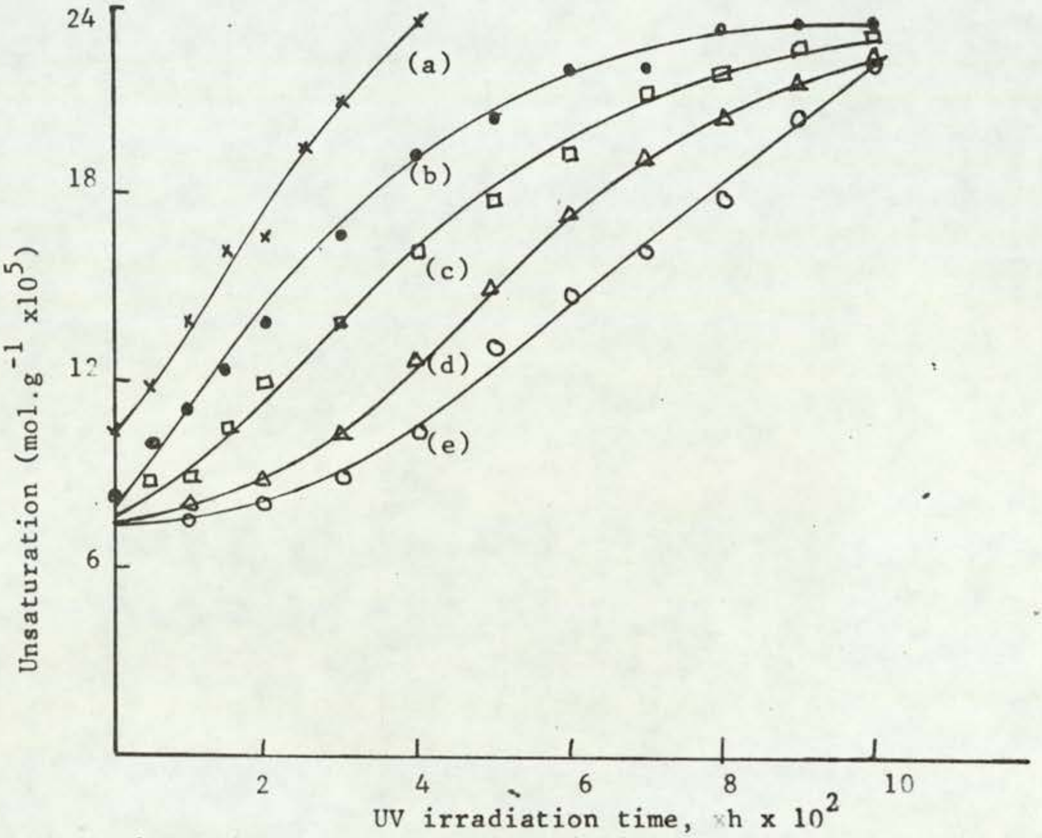


Fig.4.53: Effect of uv irradiation on unsaturation in PVC processed for 6 min. at 180°C. (a) Control; (b) Lubricants; (c) DBTM+Irg.1300 (d) DBTM+Irg.1076; (e) DBTM + Irg.1010, (2.9+2.9)X 10^{-3} mole % ; b-e with lubricants.

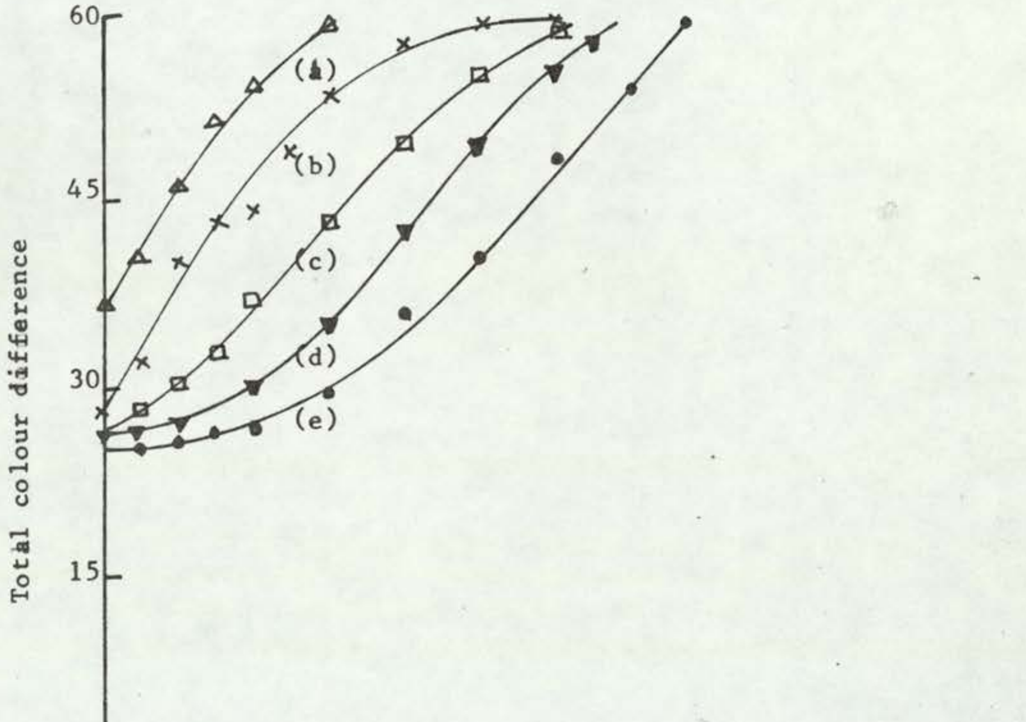


Fig. 4.54: Effect of uv irradiation on colour formation in PVC processed for 6 min. at 180°C. (a-e) as in fig. 4.54.

their behaviours during the processing operation, the stabilising effectiveness of these mixtures under photo-oxidative conditions is in the order, DBTM/Irg. 1300 DBTM/Irg.1076 DBTM/Irg.1010, indicating that the behaviours of these additives under processing conditions are in some way related to their photo-oxidative stabilising activity. For the purpose of comparison, the effects of these mixtures on unsaturation and total colour are shown together in figs. 4.53 and 54 respectively.

4.4.1 **Discussion**

The weak activities of phenolic antioxidants in combination with DBTM as photostabilisers indicate the inability of these mixtures to screen the polymer from u.v. light by absorbing the energy of the incident radiation. Also, it has been shown earlier (section 4..2.2) that the phenolic antioxidants do not synergise with DBTM during processing and that at low levels of DBTM (2.9x10^{-3} mole %), substantial concentrations of peroxides, unsaturation and colour are detected in processed PVC. The weak photo-oxidative stability of samples stabilised with the phenolic/ DBTM mixtures may therefore also be attributed to the effect of prior thermal processing.

It has been demonstrated[30,56] that the susceptibility of PVC to photo-oxidation is greatly increased by mechano-chemical processing which rapidly introduces peroxyl gel, hydroperoxides, unsaturation and carbonyl groups into the polymer, all structures capable of initiating reactions leading to photo-chemical degradation of the polymer[53,54,135]

The important role of a good thermal stabiliser in promoting photostability by preventing or reducing the formation of these prodegradant structures has been adequately recognised.[66,80,83,147]

The results discussed in this chapter show that DBTM is an effective stabiliser for PVC during processing. In combination with phenolic antioxidants, DBTM also forms effective thermal oxidative stabilising systems, however, these compounds are only weak photostabilisers for PVC. Therefore, for effective stabilisation of PVC both during processing and in service, it is desirable to incorporate photostabilisers into the stabilising formulations devised for this polymer. The improvement of the photo-oxidative stability of PVC under u.v. irradiation is discussed in Chapter 5.

CHAPTER FIVE

MELT AND PHOTO - STABILISATION OF PVC

5.1 Experimental procedure

2,2,6,6-Tetramethyl piperidine (TMPD), its derived nitroxyl radical (TMPOD) and hydroxylamine (TMPDOH), Bis (2,2,2,6-tetramethyl piperidinyl) sebacate, (Tinuvin 770, HNNH) its derived bisnitroxyl (ONNO), 1,3- Dihydroxyl-2-hydroxylmethyl-2 aminopropane (Tris Amine, TAM) and 1,3- Dihydroxyl-2 hydroxylmethyl-2- nitropropane (Tris Nitro, TN), and its stearyl, oleayl, lauryl and propionyl esters were incorporated into PVC by thermal processing in the presence of Dibutyltin maleate (DBTM). Similarly, Diphenyl nitrone, α-Phenyl-N-methyl nitrone, 2-Methyl-2 - nitroso propane (MNSP), and 2-Hydroxyl-4-octyloxybenzophenone (UV531) were processed with PVC at 180°C and the effects of all these compounds on the melt and subsequent photo-stability of PVC were investigated. The peroxide concentration, unsaturation, colour formation, gel and carbonyl index were measured at suitable intervals during the thermal processing operation and during U.V. exposure.

5.2 Results

All the stabilised formulations of PVC contain the lubricant mixture of 0.65% Wax E and 0.8g% CaSt and DBTM as a thermal stabiliser in addition to the photostabilisers investigated in this chapter.

Figures 5.1 and 2 show the effect of α-pheny -N-methyl nitrone on unsaturation and colour formation in PVC during u.v. exposure. The

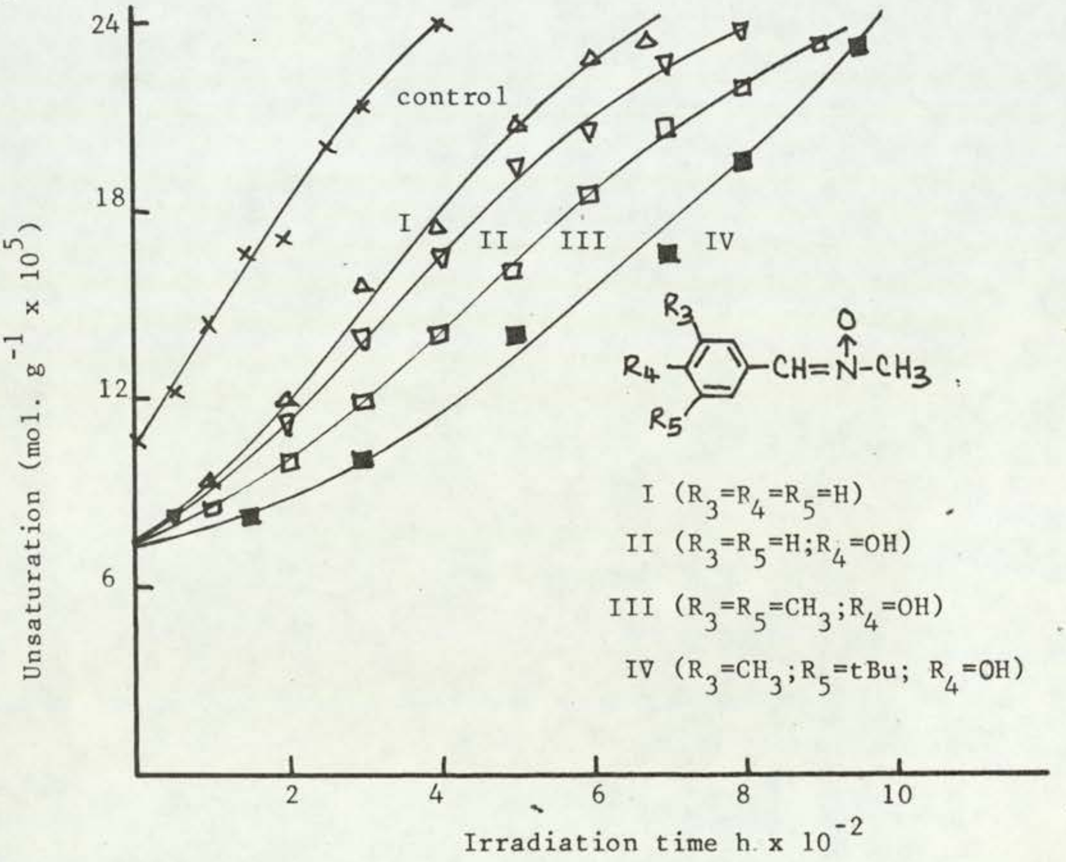


Fig. 5.1: Effect of N-phenyl nitrones on unsaturation in PVC during uv irradiation. Formulations I-IV contain lubricants (0.65% Wax E and 0.8% CaSt) and 2.9 x 10^{-3} mole % DBTM.

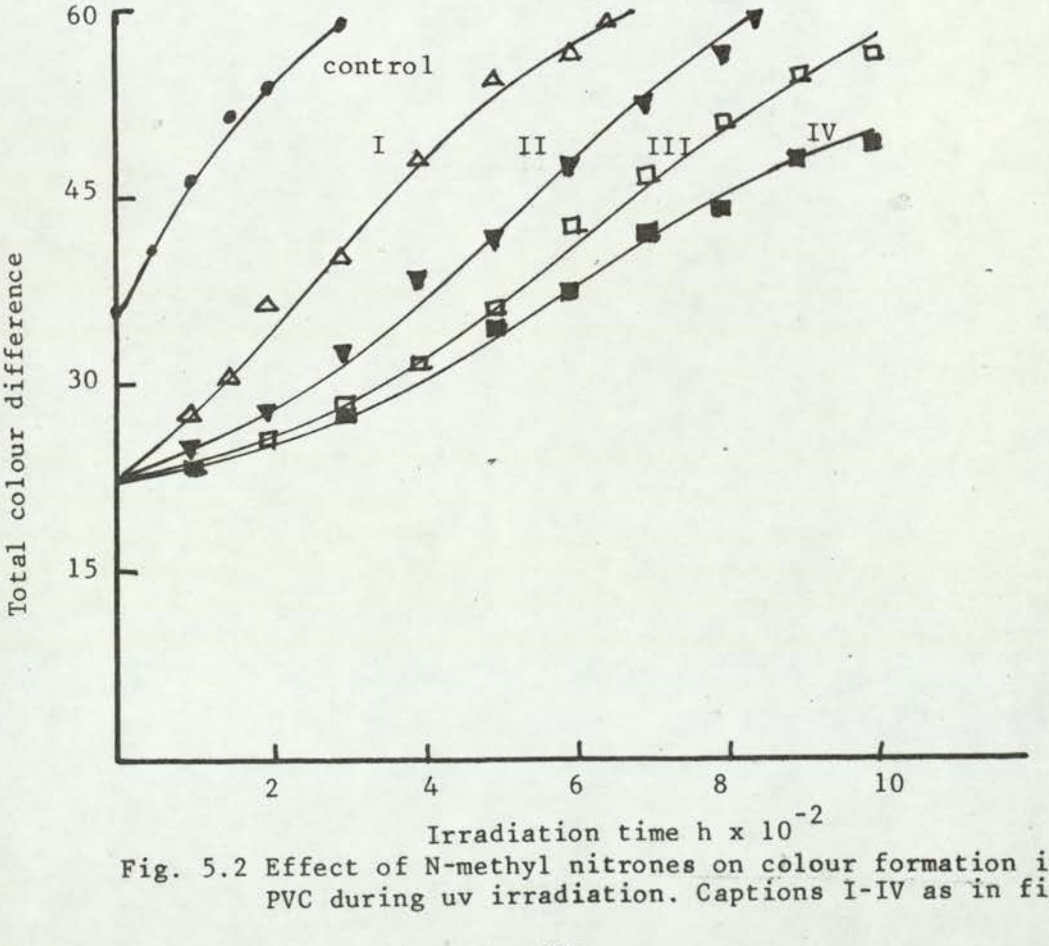


Fig. 5.2 Effect of N-methyl nitrones on colour formation in PVC during uv irradiation. Captions I-IV as in fig. 5.1

activity of the nitrones was found to increase with increasing substitution on the α-phenyl group. A similar trend was found with diphenyl nitrones (figs. 5.3 and 4). The effect of the two classes of nitrones on carbonyl index during u.v. irradiation is shown in figs. 5.5 and 6 and again, the stabilising activities was found to increase with increasing substitution on the α-phenyl group. A comparison of the N-phenyl nitrones with the N-methyl nitrones showed that the former compunds are more effective than the latter and this effect is shown in figs. 5.7 and 8. The thermal oxidative antioxidant activities of N-phenyl nitrones and N-methyl nitrones have been investigated in rubber[148] and in model compounds.[149] N-phenyl nitrones were found to be more effective than the N-methyl nitrones similar to the present results during photo-oxidation although it was found[148,149] that III and IIIA were slightly more effective than IV and IVA respectively. Although thermal degradation may not be compared directly with photo-oxidation, it appears that similar antioxidant functions may be involved in the stabilising effectiveness of these nitrones under different experimental conditions.

During the thermal processing operation, N-methyl nitrones were found to lower the concentration of hydroperoxides formed in the polymer. A similar reduction in the gel fraction of the polymer which was insoluble in dichloromethane was noticed (fig. 5.10). The similarity of the peroxide curve (fig. 5.9) and of gel (fig. 5.10) is very striking. It was shown earlier (Chapter 3) that the gel is peroxidic in nature with a strong i.r. absorption peak at $3400cm^{-1}$ which decayed rapidly under further heating or u.v. exposure (see fig. 3.8). Both peroxides and gel

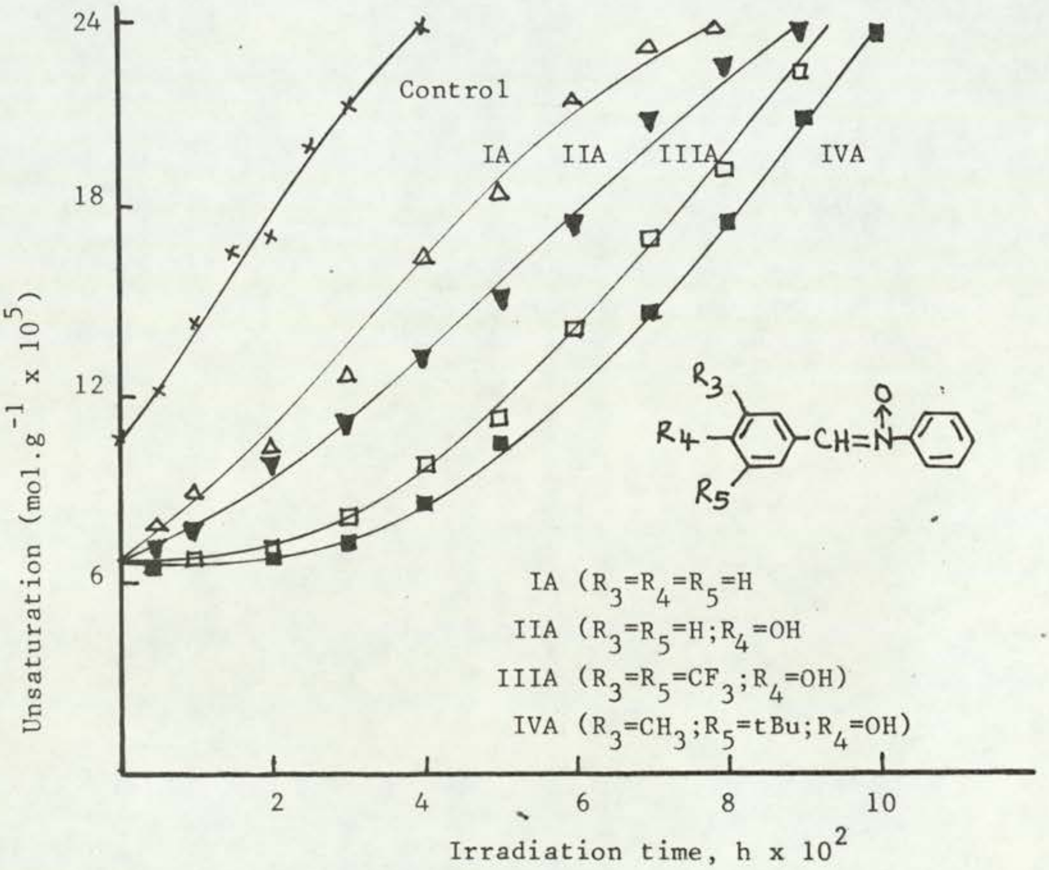


Fig. 5.3: Effect of Diphenyl nitrones on unsaturation in PVC during uv irradiation. Samples IA-IVA contain lubricants and 2.9×10^{-3} mole % DBTM.

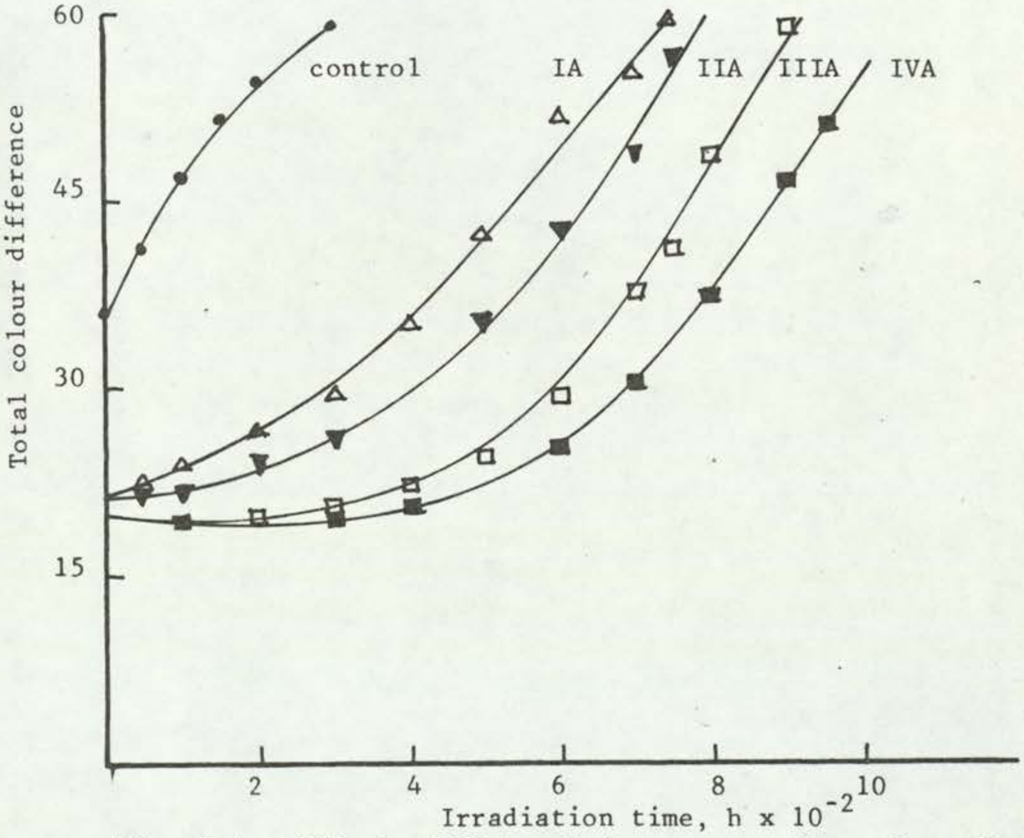


Fig. 5.4: Effect of Diphenylnitrones on colour formation in PVC during uv irradiation. Captions as in fig. 5.3

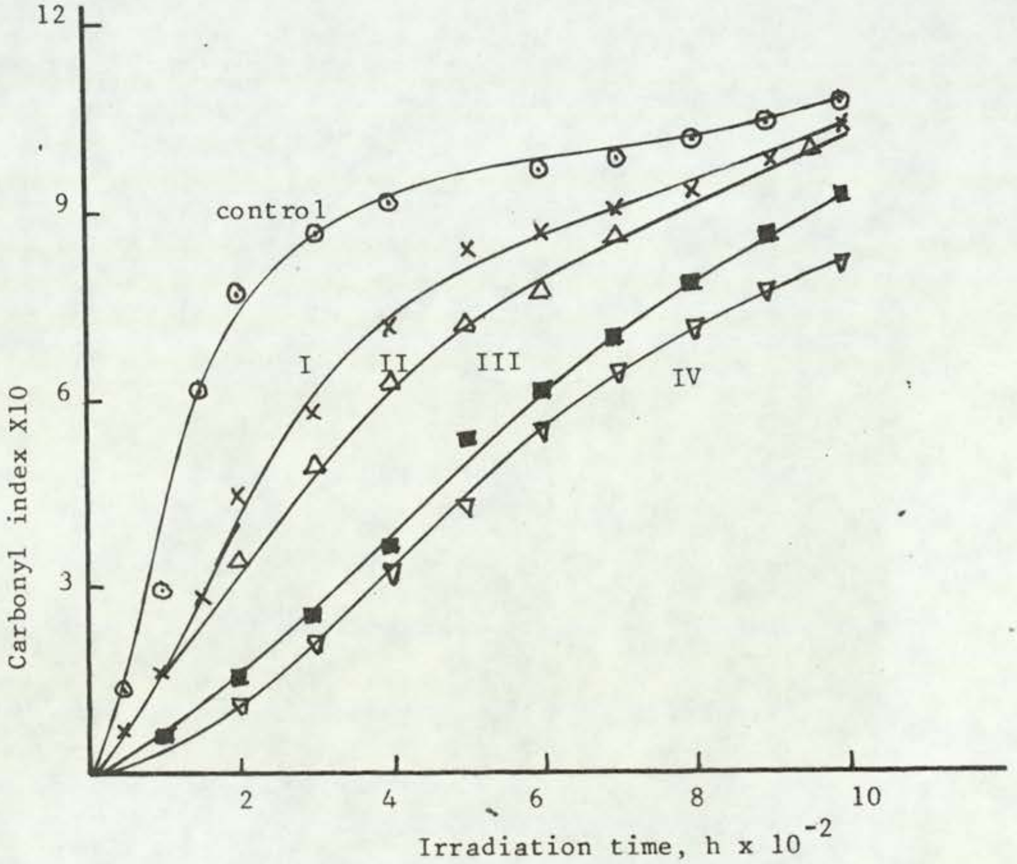


Fig. 5.5: Effect of N-methyl nitrones on carbonyl index in PVC during uv irradiation. Formulations I-IV contain lubricants and 2.9×10^{-3} mole % DBTM.

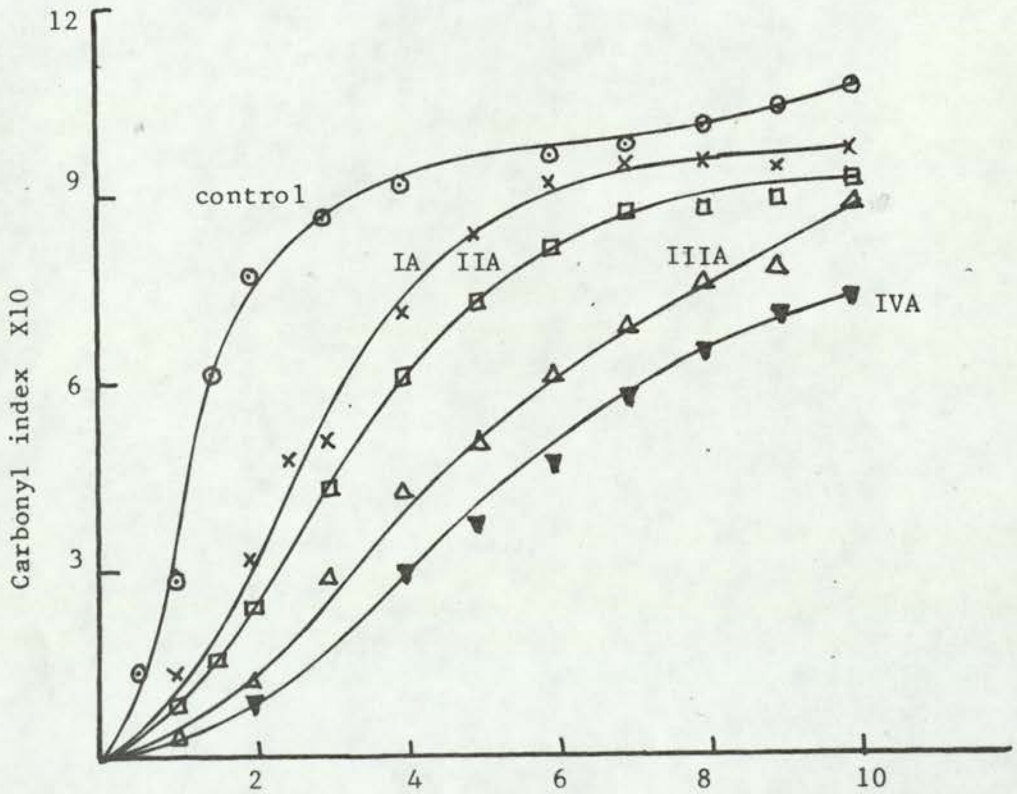


Fig.5.6: Effect of Diphenylnitrones on carbonyl index in PVC during uv irradiation. Formulations as in fig. 5.5

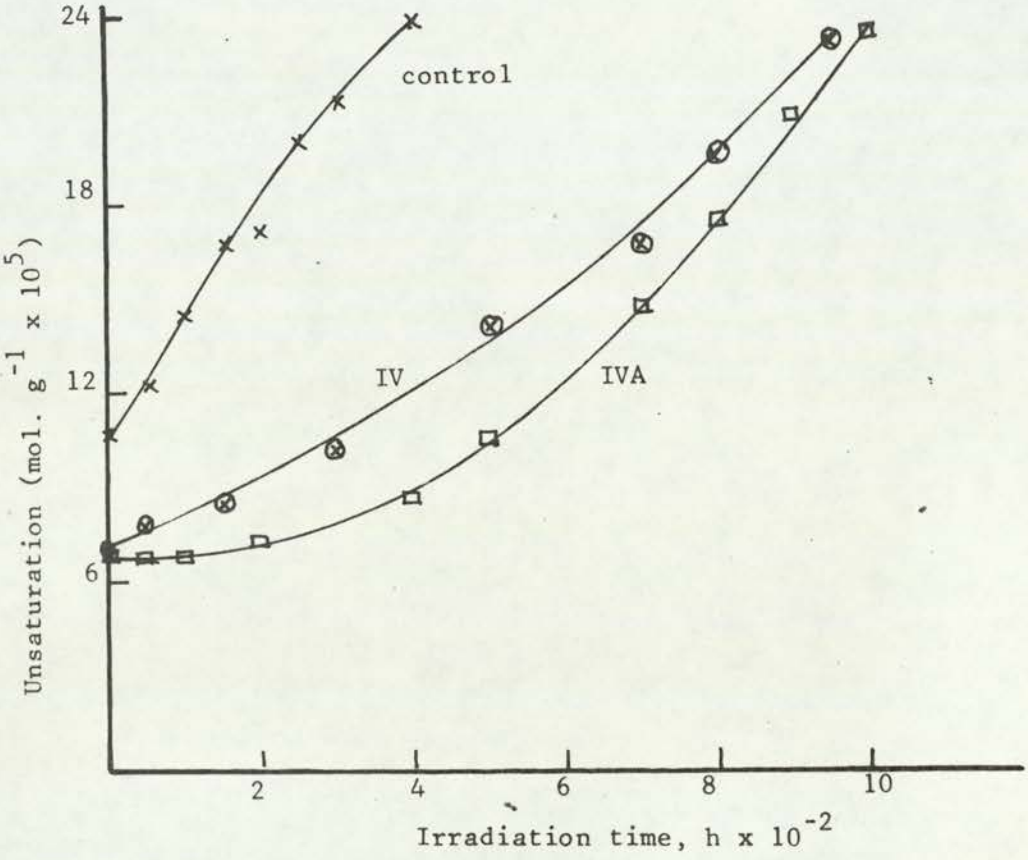


Fig. 5.7: Effect of N-methyl nitrone (IV) and Diphenyl nitrone (IVA) on unsaturation inPVC during uv irradiation. Formulations IV and IVA contain lubricants and 2.9 x 10^{-3} mole % DBTM.

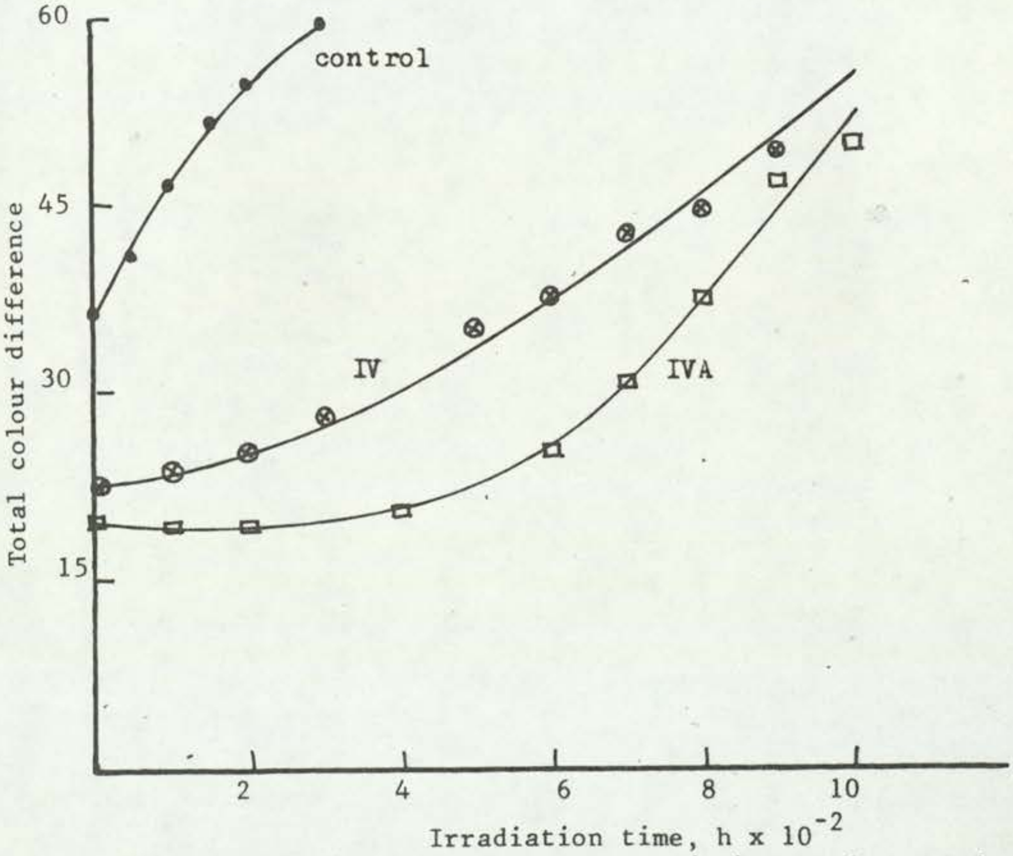


Fig. 5.8: Effect of N-methyl nitrone (IV) and Diphenylnitrone (IVA) on colour formation in PVC during uv irradiation. Formulations as in fig. 5.7

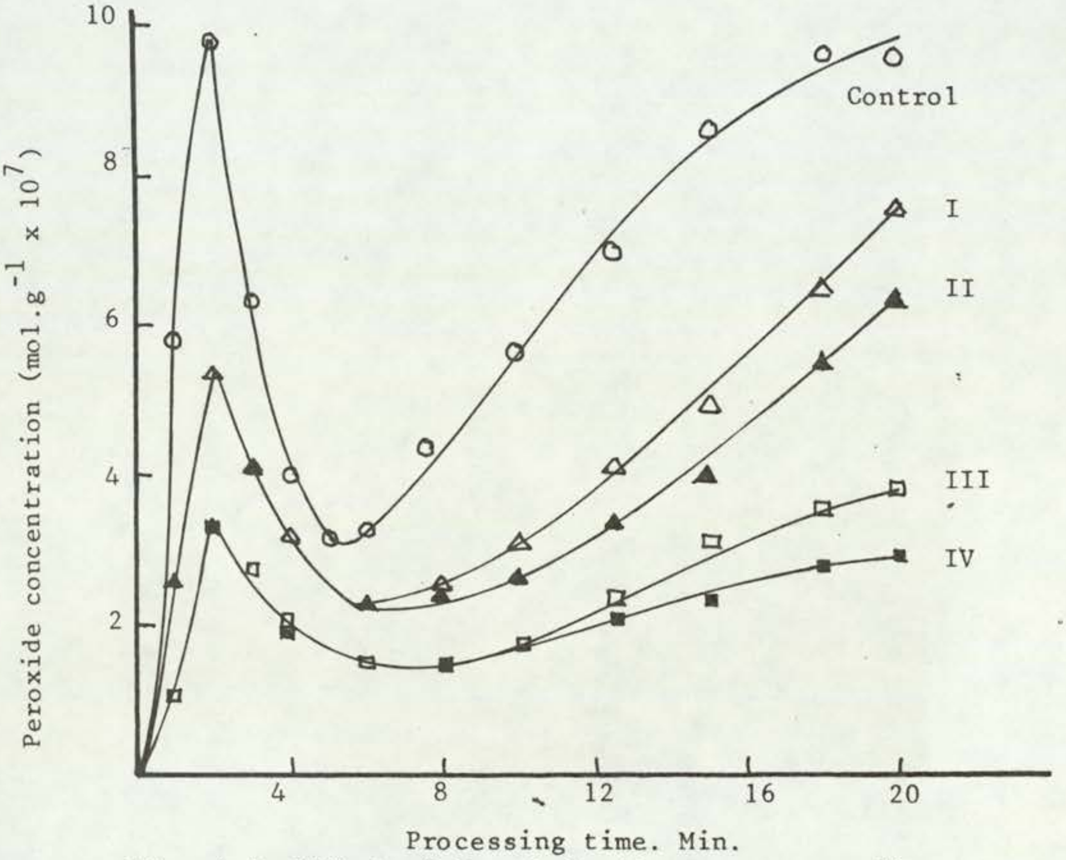


Fig. 5.9: Effect of N-methyl nitrones on peroxide concentration in PVC during thermal processing at 180°C. Formulations contain lubricants and 2.9 x 10^{-3} mole % DBTM.

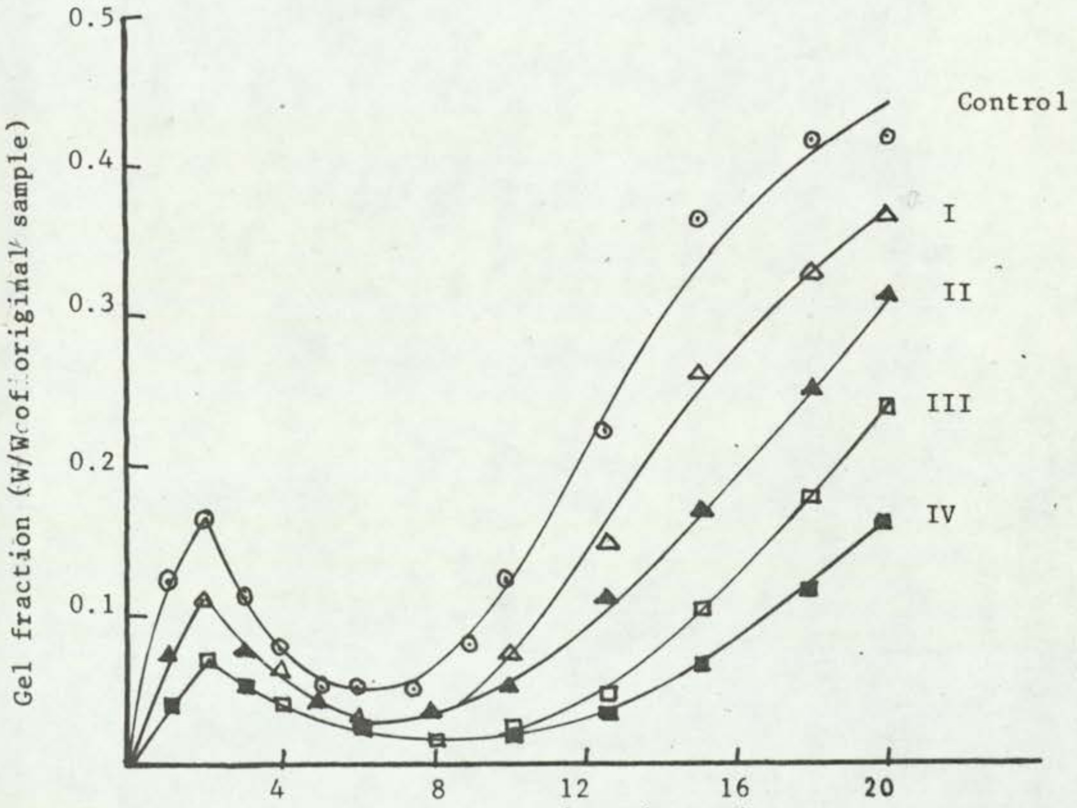
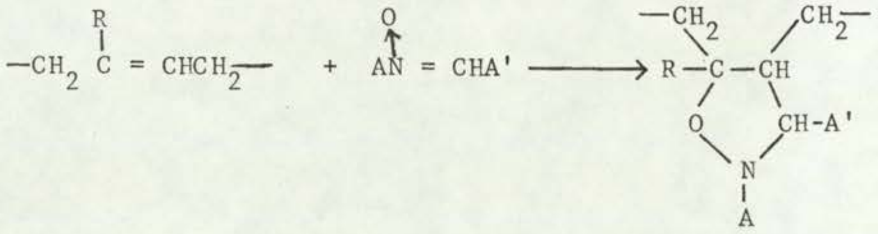


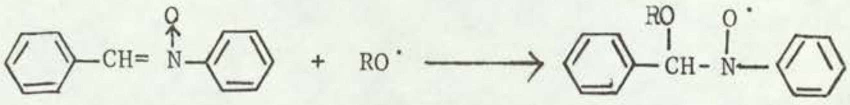
Fig. 3.10: Effect of -Phenyl-N-methyl nitrone on gel formation in PVC during thermal processing at 180°C. I-IV as in fig. 5.9

fraction were also reduced by N-phenyl nitrones (fig. 5.11 and 12); their effects were also found to increase with increasing electron-donor activities of the substituents.

It has been shown[150,151] that the nitrone group represents a potentially versatile reagent for double bonds by the 1,3-cycloaddition reaction (1).


(1)

1,3 cycloaddition of nitrones to both unconjugated[152,153] and conjugated unsaturation[154] have been reported. It is also known[155,157] that nitrones are effective trapping agents for alkoxy radicals, giving rise to a stable nitroxyl radical which is itself an effective alkyl radical trap (2). It has also been demonstrated[149] that nitrones effectively destroy hydroperoxides in model systems and


(2)

since the concentration of hydroperoxides in PVC samples stabilised with nitrones is lower than in unstabilised samples (figs. 5.9 and 11), it is clear from these results that nitrones also destroy hydroperoxides in the solid polymer. The stabilising effect of both N-phenyl and N-methyl nitrones in reducing the concentration of hydroperoxides and carbonyl formation is therefore consistent with the fact that apart from acting as free radical traps[155,157] they also function as hydroperoxide decomposers.[149]

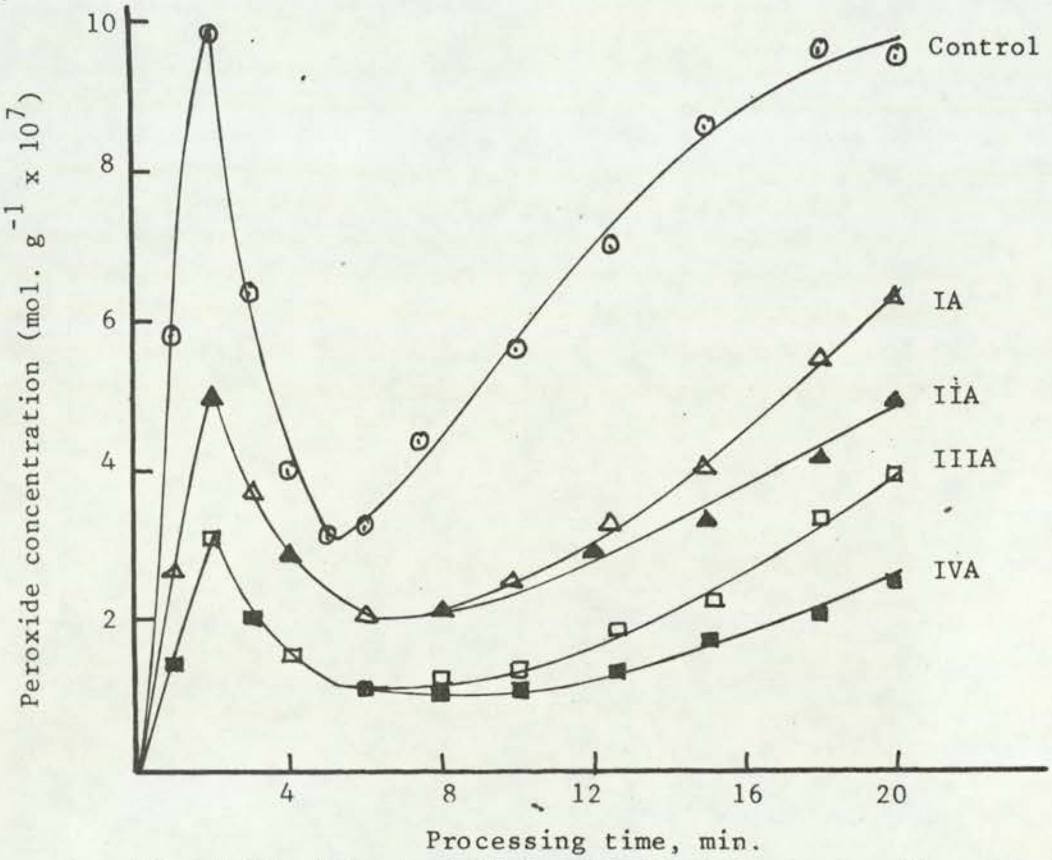


Fig. 5.11: Effect of Diphenyl nitrones on peroxide concentration in PVC during thermal processing at 180°C. Formulations IA-IVA contain lubricants and 2.9 x 10^{-3}M

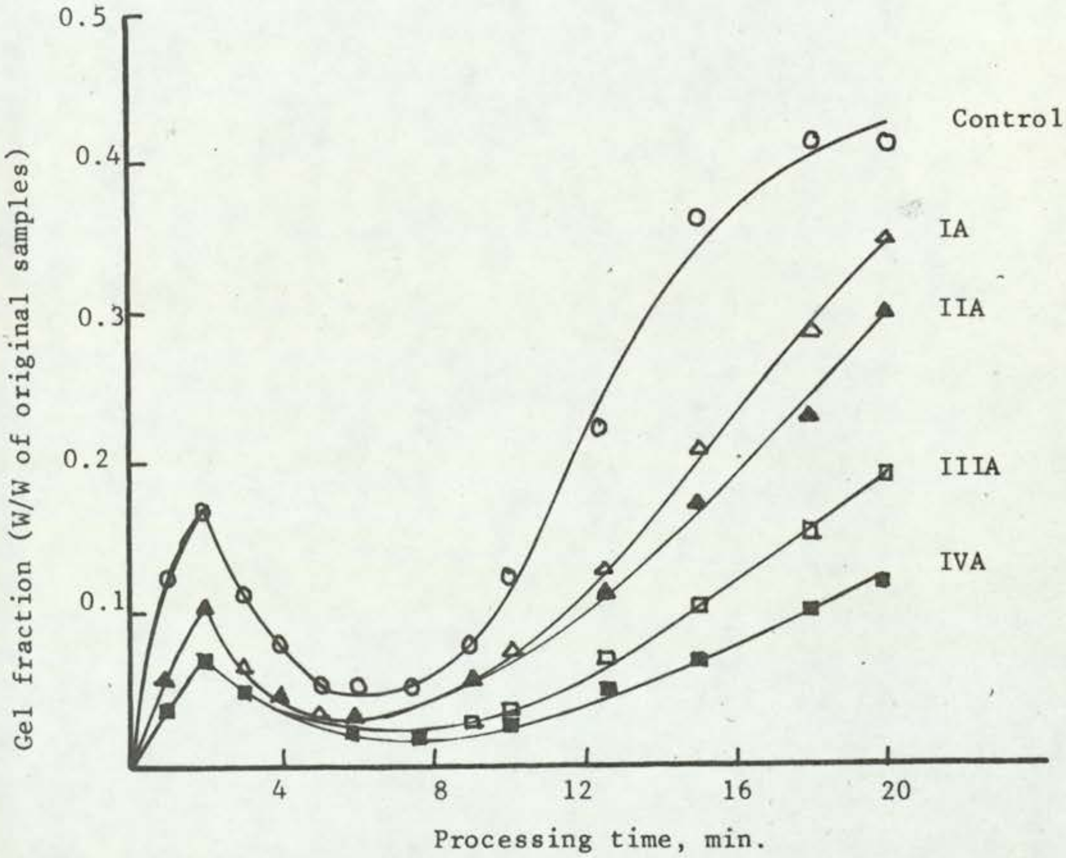


Fig. 5.12: Effect of Diphenyltrones on gel formation in PVC during thermal processing at 180oC, IA - IVA as in fig. 5.11.

The concentration of both unsaturation and total colour formed is higher in the presence of N-methyl nitrones (figs. 5.7 and 8) than N-phenyl nitrones suggesting that the earlier compounds react less effectively with double bonds (or do not at all[148]) than the latter compounds.

Figure 5.13 compares the effect of 2-methyl-2-nitroso propane (MNSP) on hydroperoxide concentration with that of hindered piperidine compounds. It can be seen that the highest concentration of hydroperoxides accumulated in the unstabilised sample during processing. The additional incorporation of 0.2×10^{-3} mole % MNSP to PVC stabilised with 2.9×10^{-3} mole % DBTM caused a further reduction in the concentration of hydroperoxides. It can be seen that TMPD is more effective than MNSP at the same molar concentration whereas the derived nitroxyl TMPDO and hydroxylamine TMPDOH appeared to be equally effective as the parent amine TMPD in reducing hydroperoxides. The corresponding effect of these stabilisers on gel fraction formed in the polymer is shown in fig. 5.14.

The development of unsaturation and colour formation during irradiation of samples stabilised with a mixture of DBTM and MNSP, TMPD, TMDPO and TMPDOH is shown in figs. 5.15 and 16. These curves show that the DBTM/MNSP mixture is inferior to the DBTM/hindered piperidines under photo-oxidative conditions. Figures 5.17 and 18 show the effect of varying concentrations of MNSP and TMPD on carbonyl group formation in PVC during irradiation. The curves demonstrate a two-stage development in the accumulation of carbonyl groups. An earlier rapid rate of carbonyl

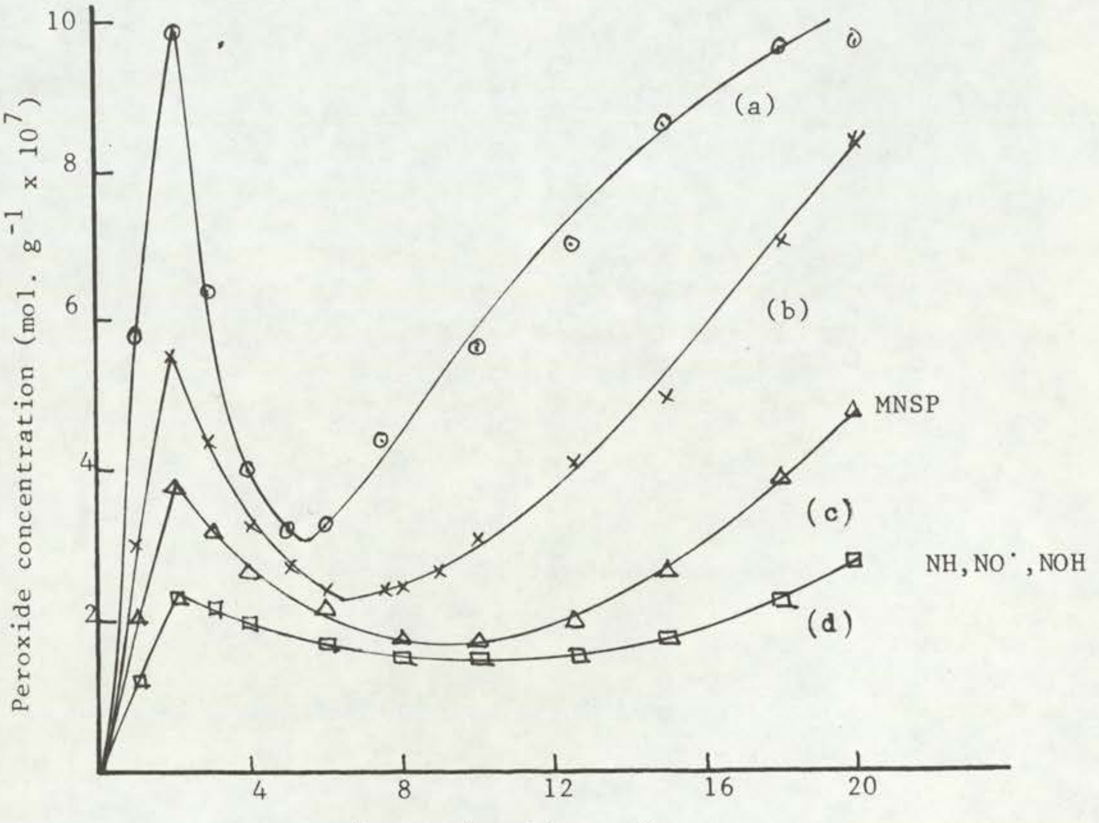


Fig. 5.13: Effect of thermal processing at 180^{o}C on peroxide concentration in PVC, (a) control; (b) 2.9x10^{-3}M DBTM (c) MNSP (d) DBTM/TMPD, DBTM/TMPDO and DBTM/TMPDOH, (2.9/0.1)x10^{-3}M. Formulations b-d contain lubricants.

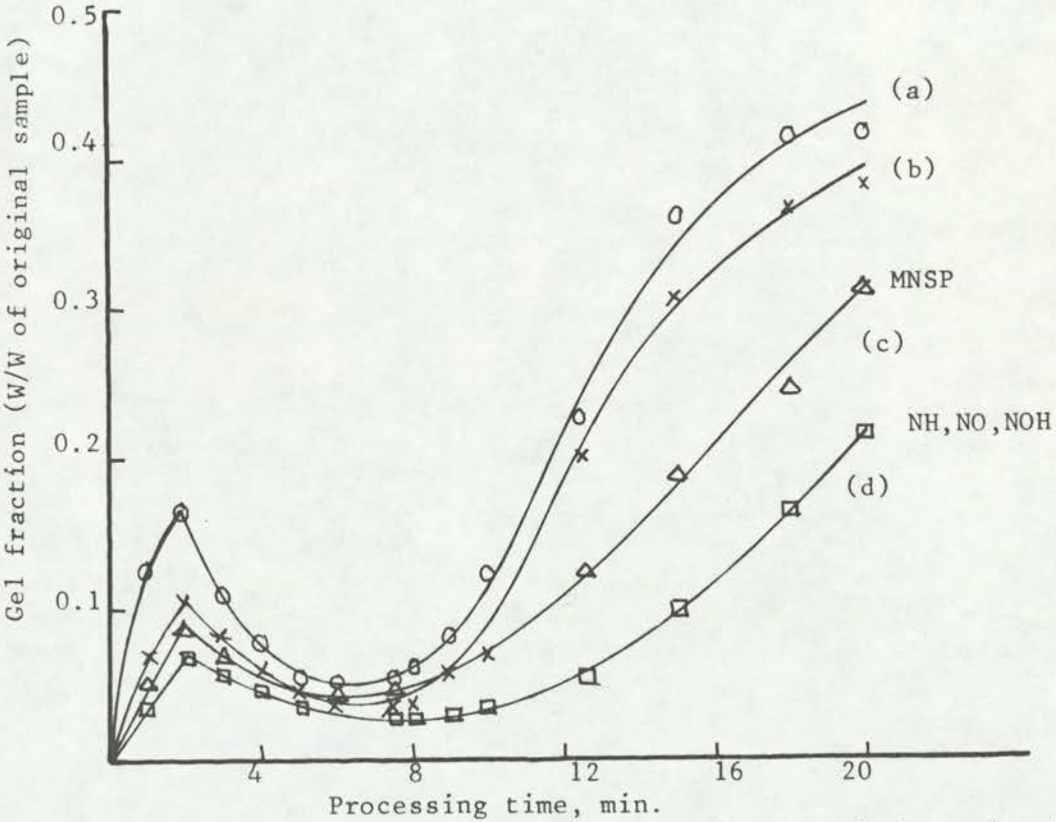


Fig. 5.14: Effect of thermal processing on gel formation in PVC (a-d) as in fig. 5.13.

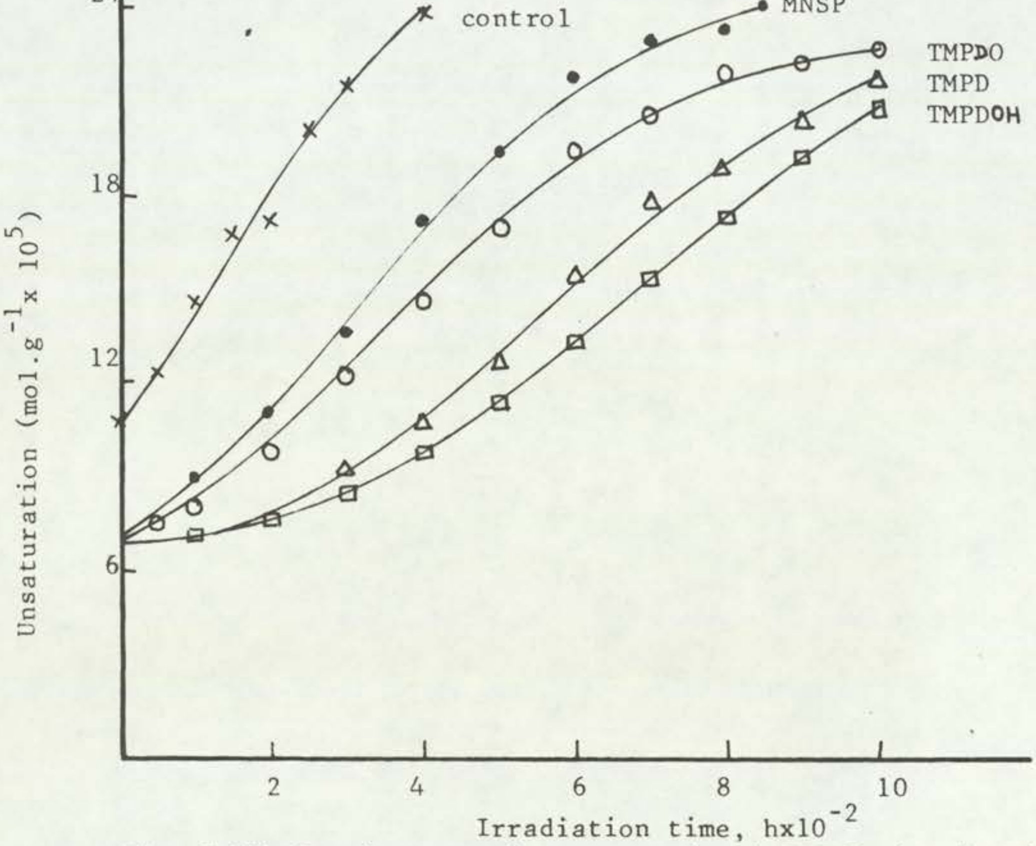


Fig. 5.15: Development of unsaturation inPVC during irradiation, stabilised samples contain 2.9x10^{-3}M DBTM and 0.2x10^{-3}M of uv stabiliser shown.

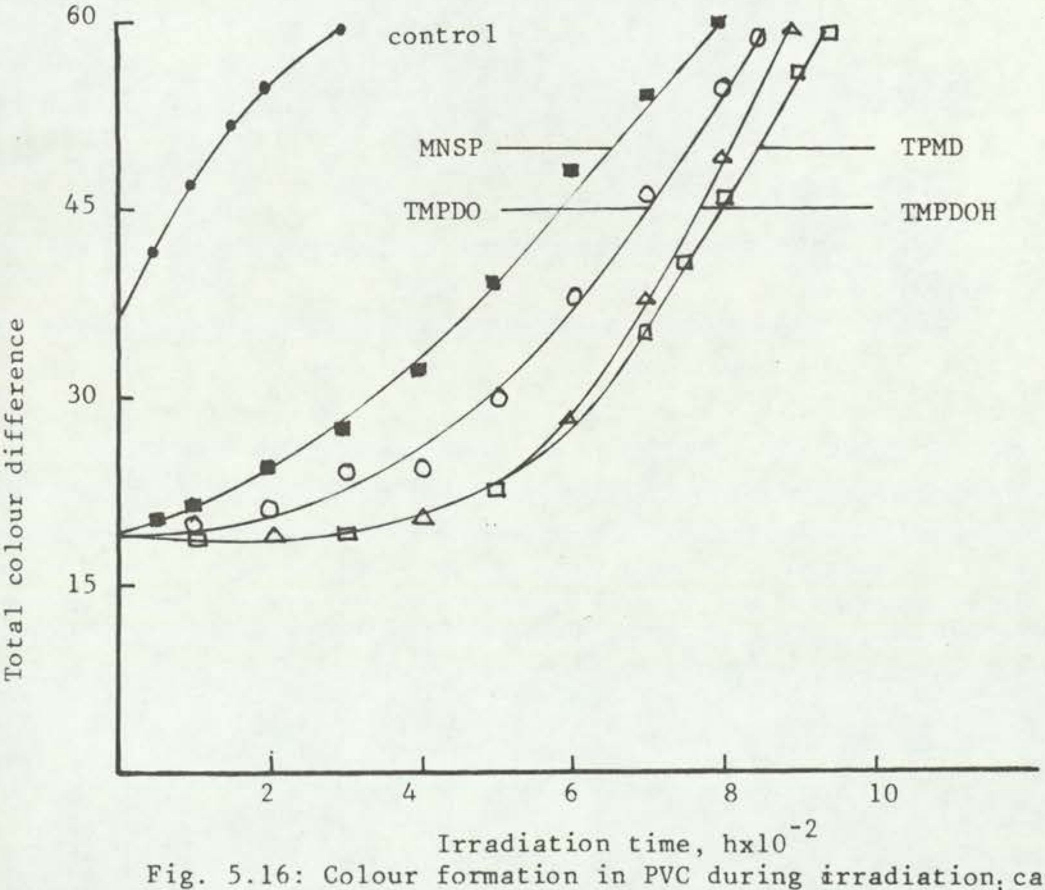


Fig. 5.16: Colour formation in PVC during irradiation, captions as in fig. 5.15.

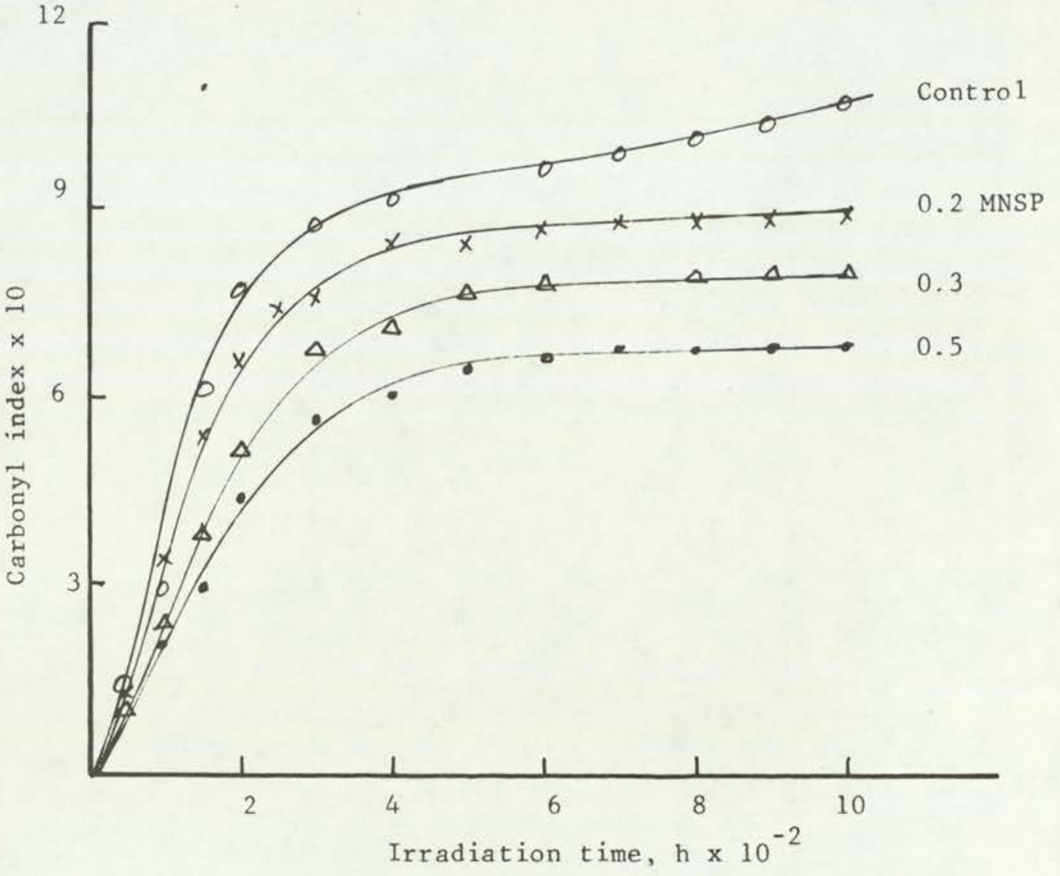


Fig. 5.17: Effect of varying concentrations of MNSP on carbonyl index during irradiation of PVC. Stabilised samples contain lubri-atns and 2.9×10^{-3} mole % DBTM.

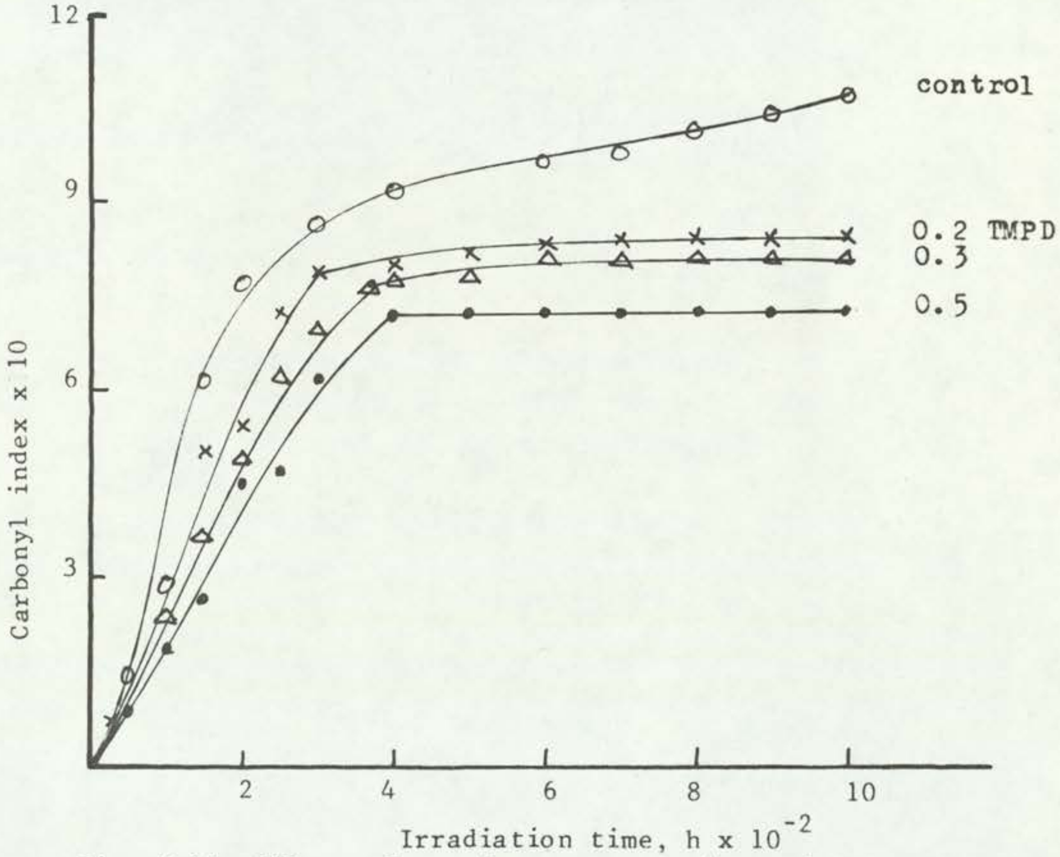


Fig. 5.18: Effect of varying concentrations of TMPD on carbonyl index during irradiation of PVC. Formulations as in fig. 5.17.

accumulation was followed by a second stage of a much slower rate of further increase. Unlike the unstabilised sample, carbonyl concentration in stabilised formulations appears to reach equilibrium shortly after a rapid increase in the first stage. The activity of both MNSP and TMPD were found to increase with increasing concentration in the range 2 to 5 x 10^{-4} mole%. Similar behaviours are obtained in the presence of HNNH (fig. 5.19) and TMPDOH (fig. 5.20).

Figures 5.21 and 22 compare the effect of tris nitro (TN) with the mono-piperidine stabilisers (TMPD, TMPDO, TMPDOH), and the bis-piperidine stabilisers (HNNH and ONNO) on hydroperoxide concentration and gel respectively. The mono-piperidine compounds are found to be more effective than TN, but are themselves less effective than the bis-piperidine compounds. The latter result is due, at least in part, to the bifunctionality of HNNH and ONNO although their molecular weights may also contribute to the observation. However, Vink[158] has suggested that physical processes, such as volatilisation and exudation generally contribute only to a minor extent to loss of u.v. stabilisers in polyolefins.

The evidence in fig. 5.23 suggests a strong effect of both HNNH and ONNO on hydroperoxides in that the additional presence of 0.2x10^{-3} mole % of the uv stabilisers substantially reduced hydroperoxide concentration than the level found in formulations stabilised with 2.9 x 10^{-3} mole % DMTM. A similar effect on the solvent-insoluble gel fraction of the polymer is shown in fig. 5.24. The effect of both the bis piperidine (HNNH) and its derived nitroxyl radical (ONNO), and the mono piperidine

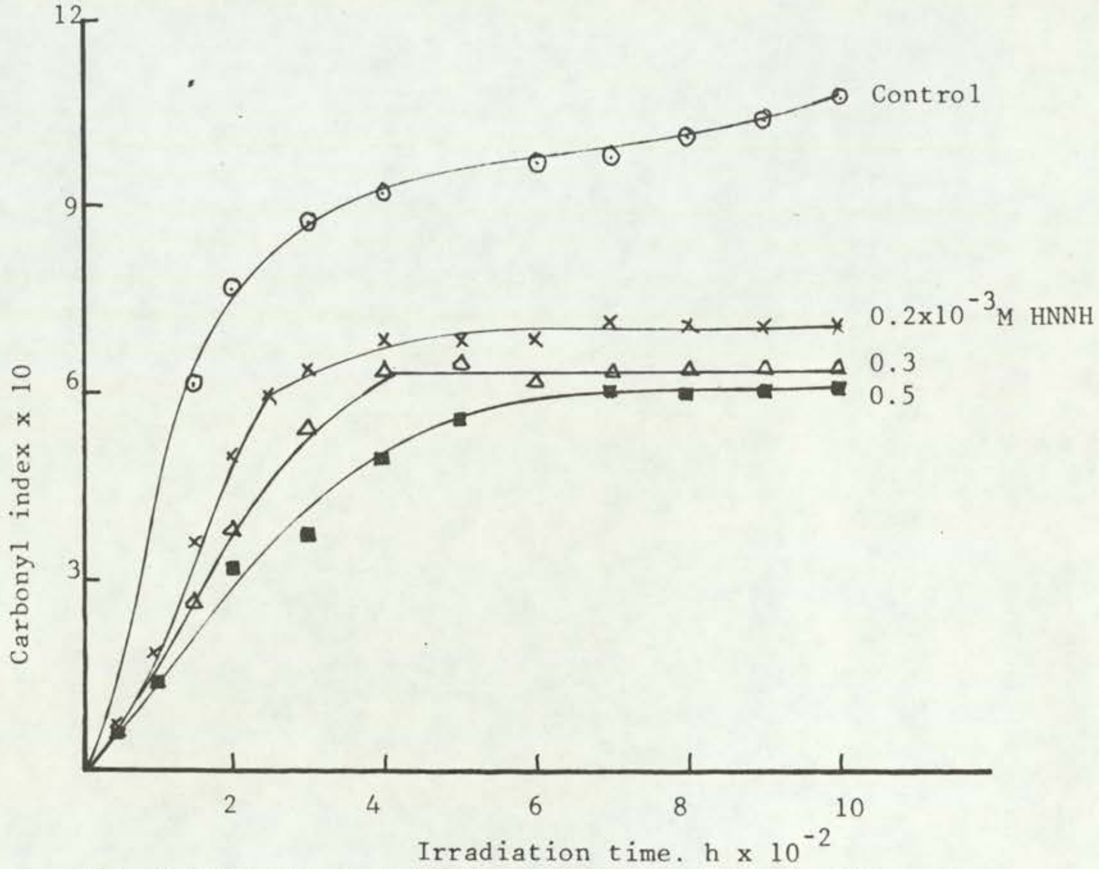


Fig. 5.19: Effect of HNNH on carbonyl index in PVC during uv irradiation stabilised samples contain lubricants and 2.9×10^{-3} mole % DBTM.

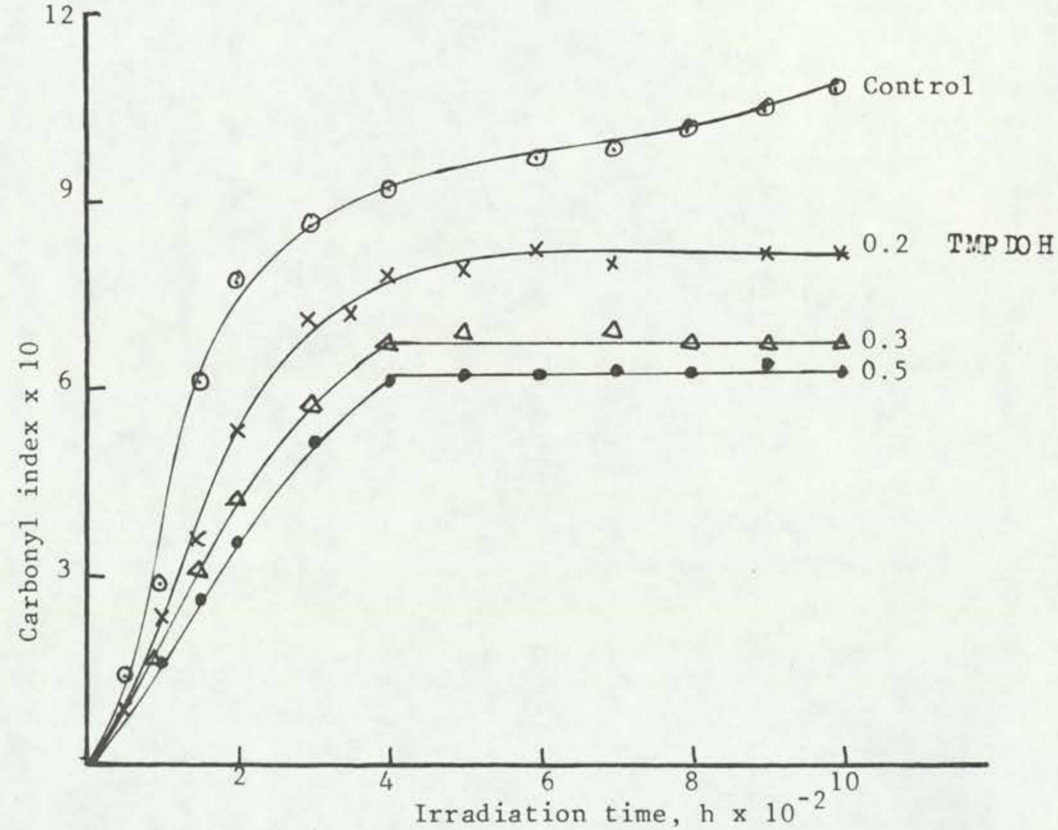


Fig. 5.20: Effect of TMPDOH on carbonyl index in PVC during uv irradiation. Formulations as in fig. 5.19.

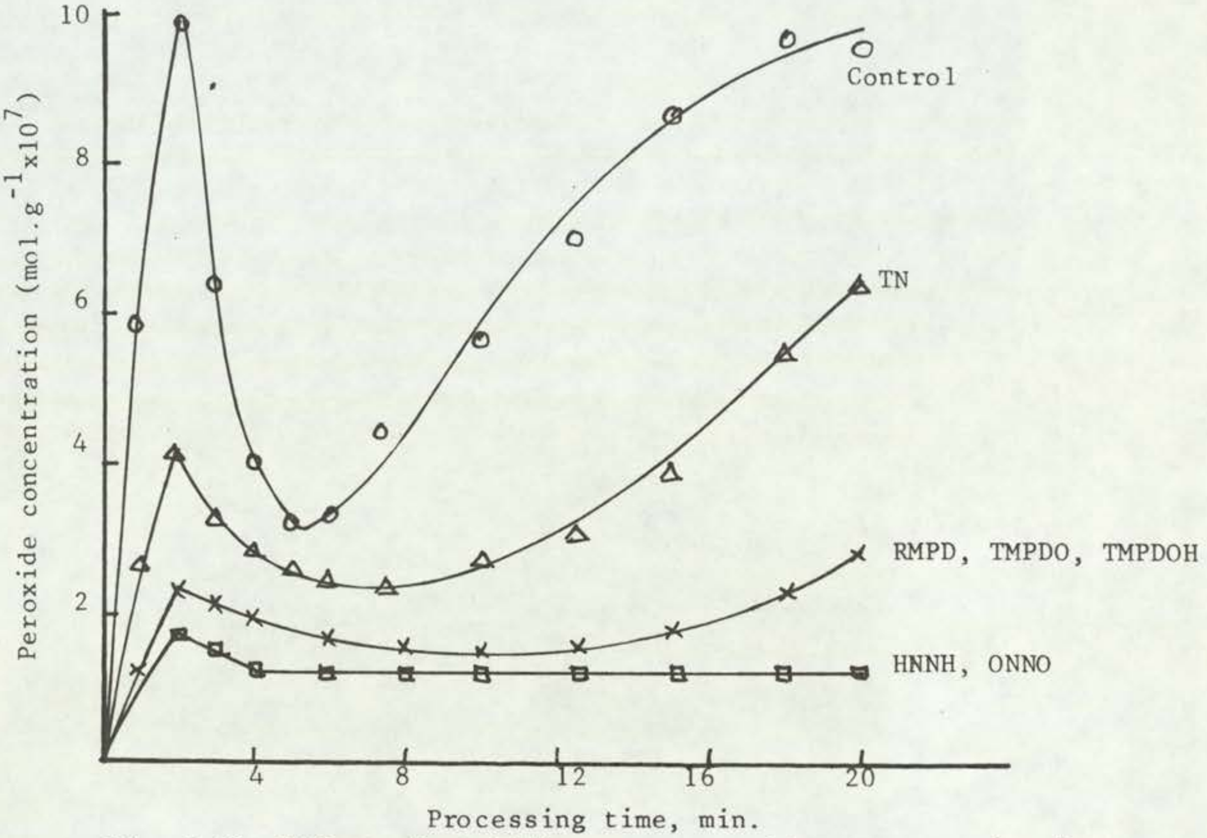


Fig. 5.21: Effect of stabilisers on peroxide concentration in PVC during thermal processing at 180^{o}C. Formulations contain $2.9\mathrm{x}10^{-3}$ mole% DBTM, $0.2\mathrm{x}10^{-3}$ mole % uv stabilisers shown and lubricants.

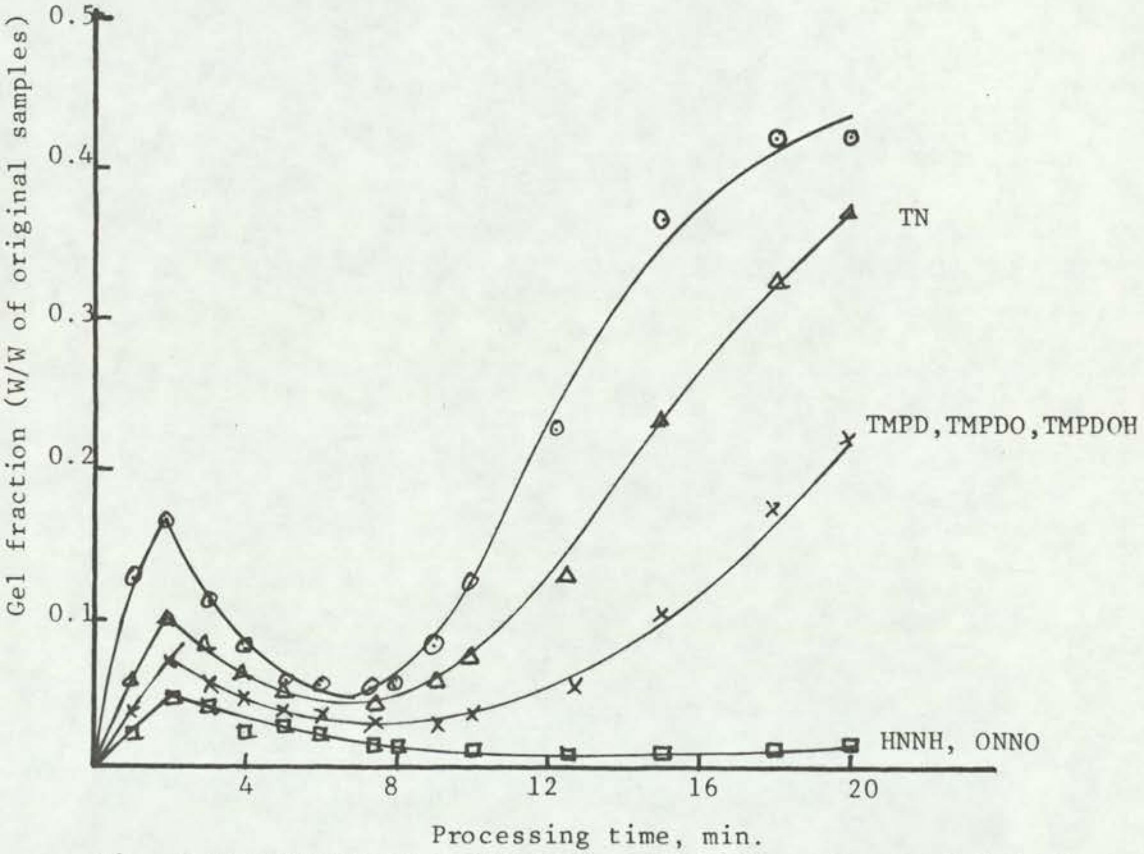


Fig. 5.22: Effect of stabilisers on gel formation in PVC during thermal processing at 180^{o}C. Formulations as in fig. 5.21.

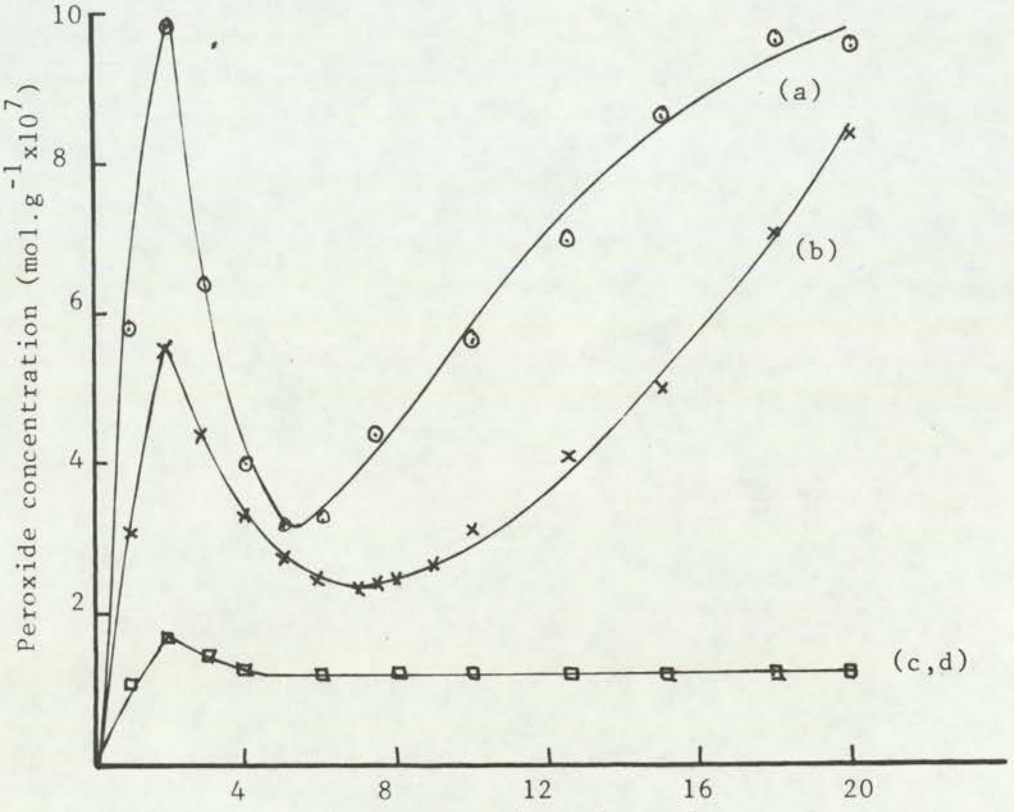


Fig. 5.23: Effect of thermal processing at 180°C on peroxide concentration in PVC. (a) Control. (b) 2.9x10^{-3} mole % DBTM; (c) DBTM/HNNH; (d) DBTM/ONNO. (C,d) 2.9x0.2) Stabilised samples contain lubricants.

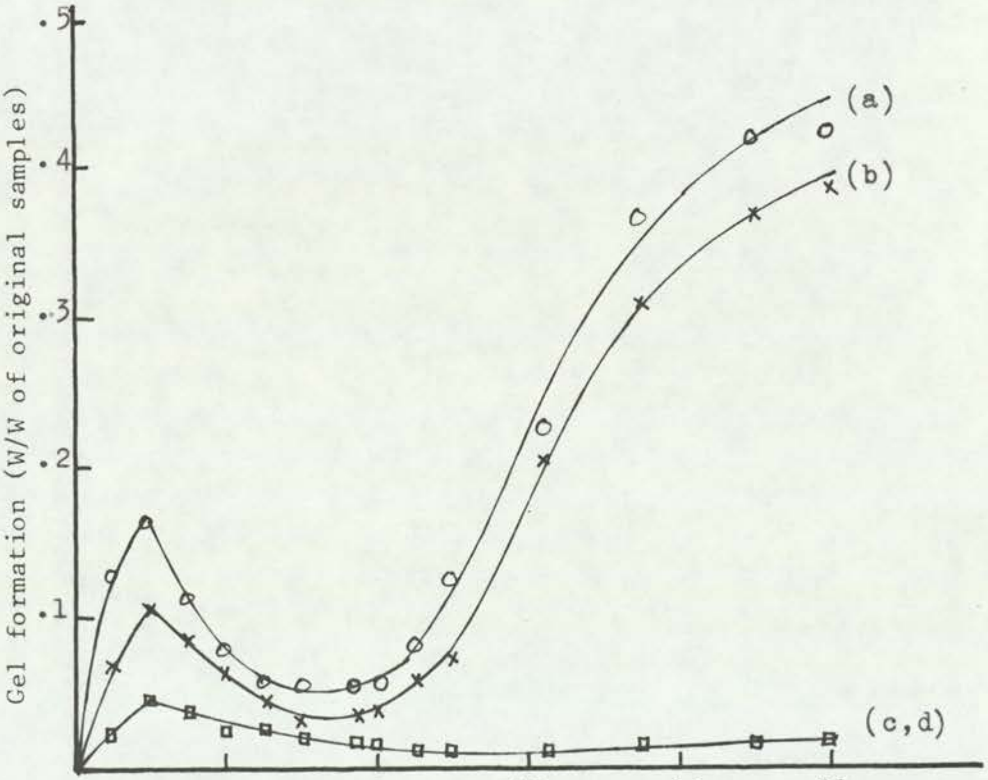
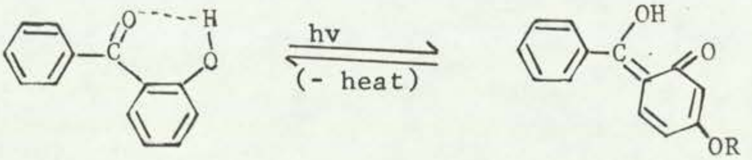


Fig. 5.24: Effect of thermal processing at 180°C on gel formation in PVC. Captions (a-d) as in fig. 5.23

(TMPD) and its derived nitroxyl radical (TMPDO) and hydroxylamine (TMPDOH) on carbonyl index in PVC is shown in figs. 5.25 and 26. It is seen from these curves that the bis nitroxyl is slightly more effective than its parent amine (fig. 5.25) while the corresponding nitroxyl radical and hydroxylamine are similarly slightly more effective than their parent amine (TMPD). It is significant to notice that the activities of the parent amine and its resulting derivative(s) are quite similar, indicating that these stabilisers function by similar mechanisms. This aspect is discussed further later.

The activities of 2-hydroxyl-4-octyloxy benzophenone (UV 531) in reducing unsaturation, colour formation, hydroperoxides, gel formation and carbonyl index in PVC are compared with the hindered amine stabilisers (TMPD) and HNNH) in figs. 5.27-31 respectively. The uv absorption and photostabilisation characteristics of derivatives of 2-hydroxy benzophenone are known to be due to their highly conjugated structure and to their intramolecular hydrogen bonding[125]. The transfer of uv energy to less dangerous low-energy quanta is accomplished by the ability of these stabilisers to rearrange into a quinoid structure[159], which reverts back to the original structure by giving up the acquired energy in the form of heat (3).



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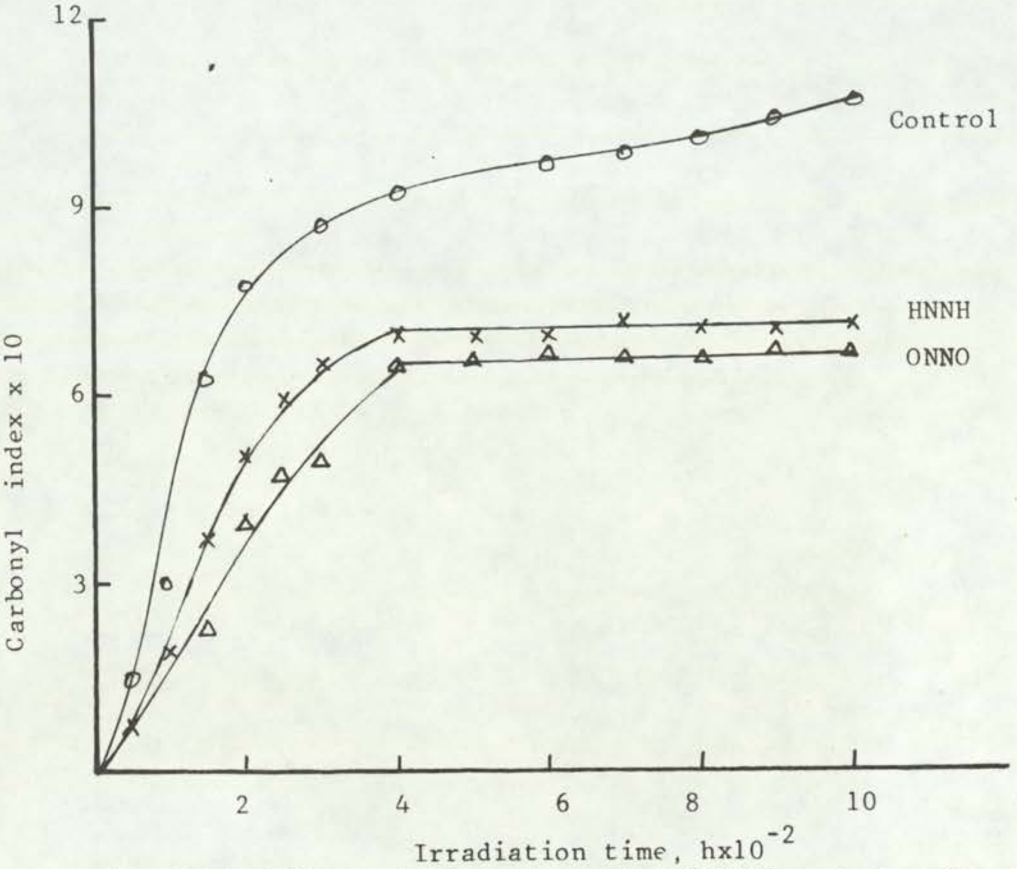


Fig. 5.25: Effect of bis- piperidine (HNNH) and its nitroxyl radical (ONNO) on carbonyl index in PVC during irradiation Formualtions contain 2.9×10^{-3} mole % DBTM, 0.2×10^{-3} (HNNH, ONNO) and lubricants.

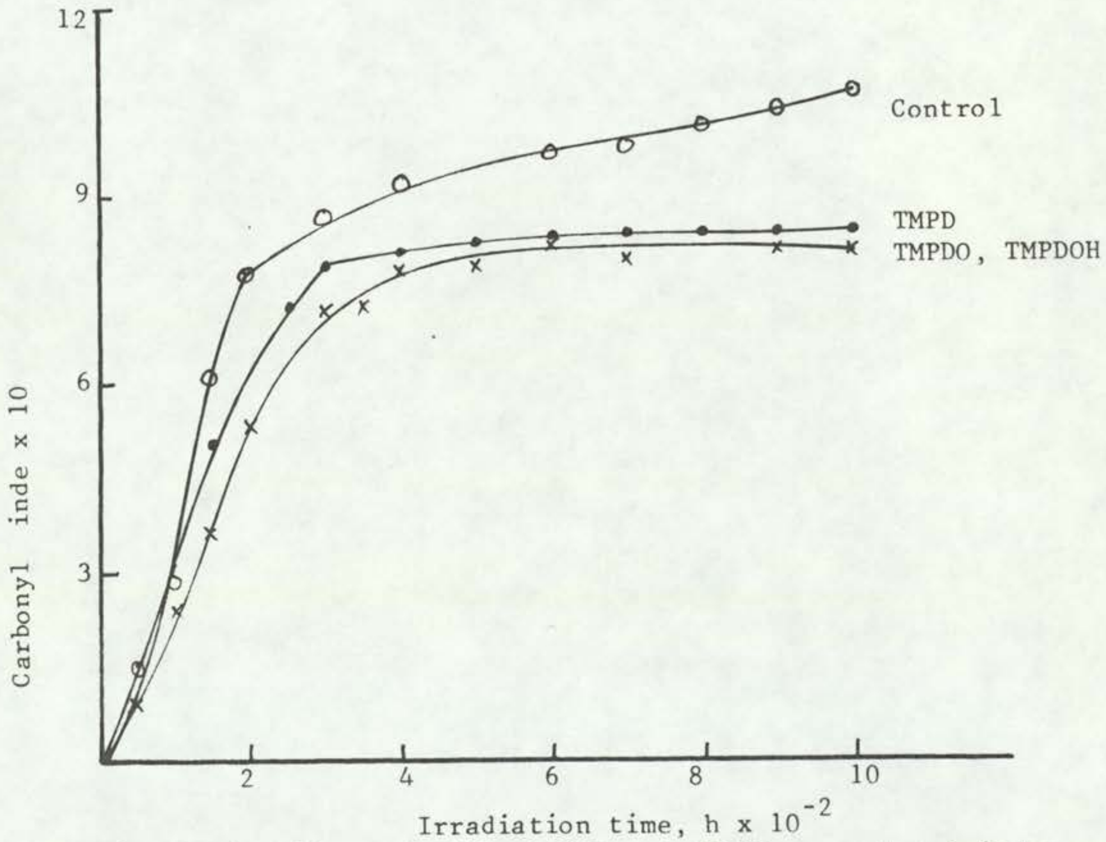


Fig. 5.26: Effect of TMPD, TMPDO and PMDOH on carbonyl index during uv irradiation. Captions asin fig. 5.25.

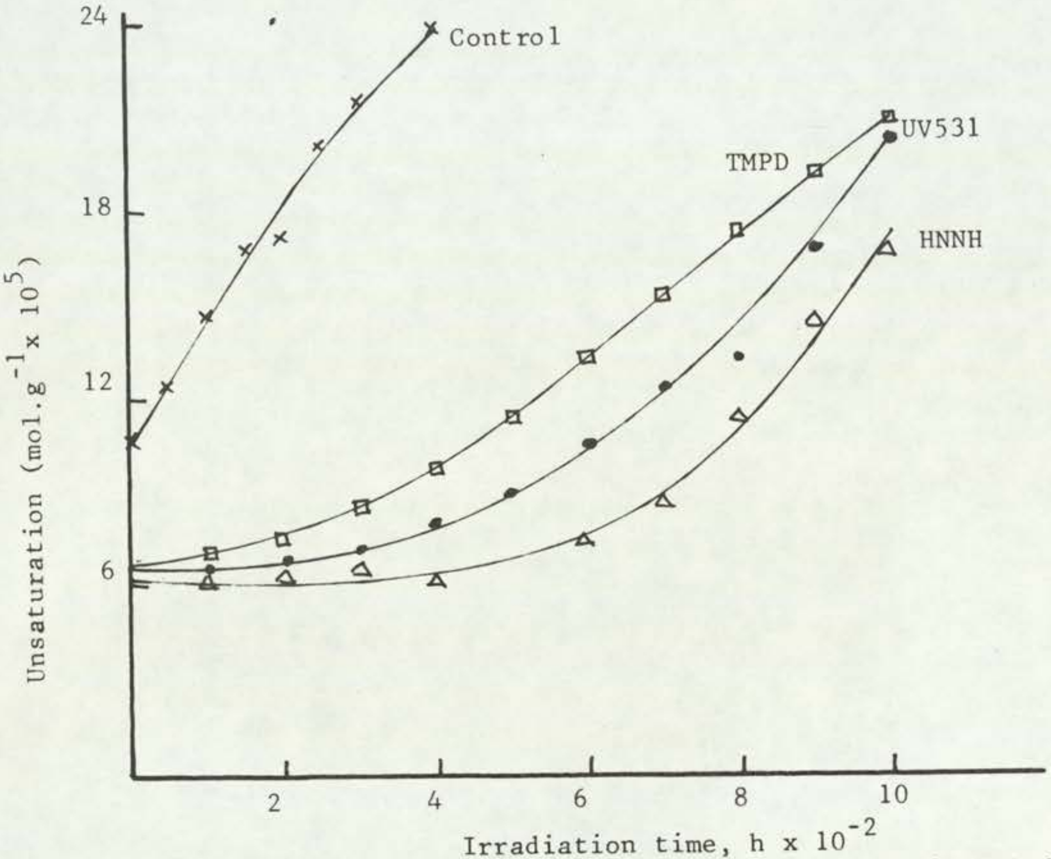


Fig. 5.27: Effect of stabilisers on unsaturation in PVC during irradiation. (Formulations contain 2.9×10^{-3} mole % DBTM, 0.2×10^{-3} mole % uv stabilisers and lubricants.)

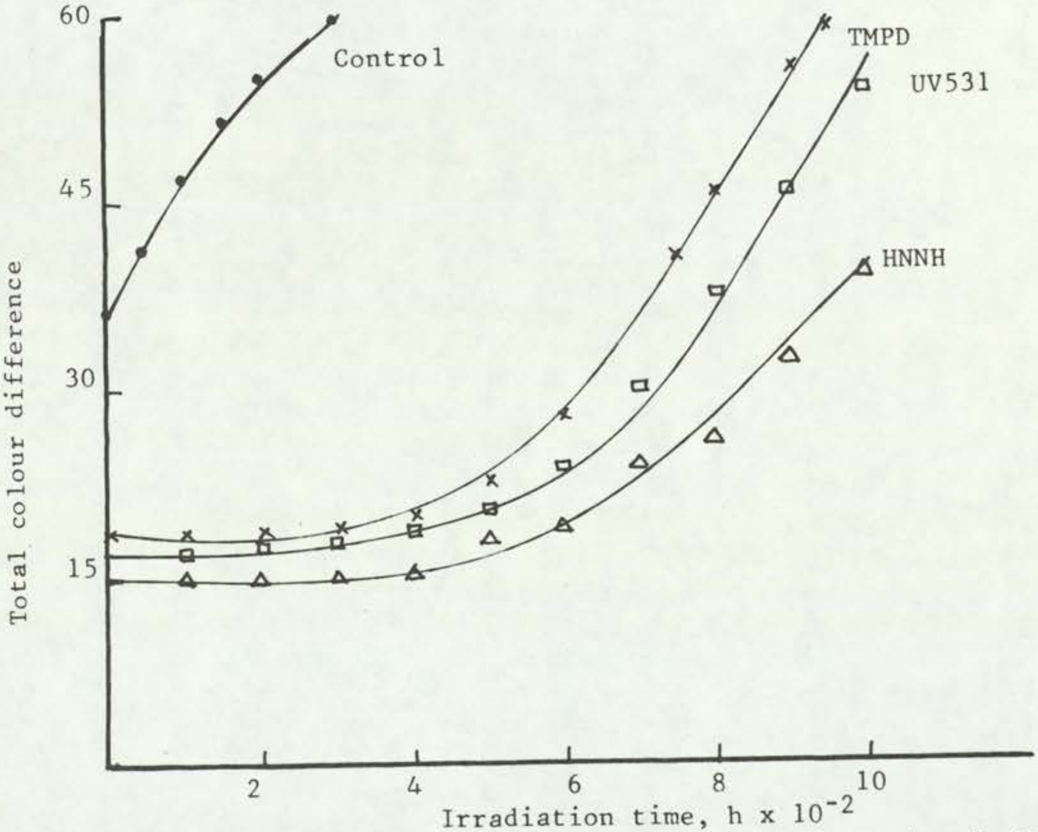


Fig. 5.28: Effect of stabilisers on colour formation in PVC during irradiation (Formulations as in fig. 5.27)

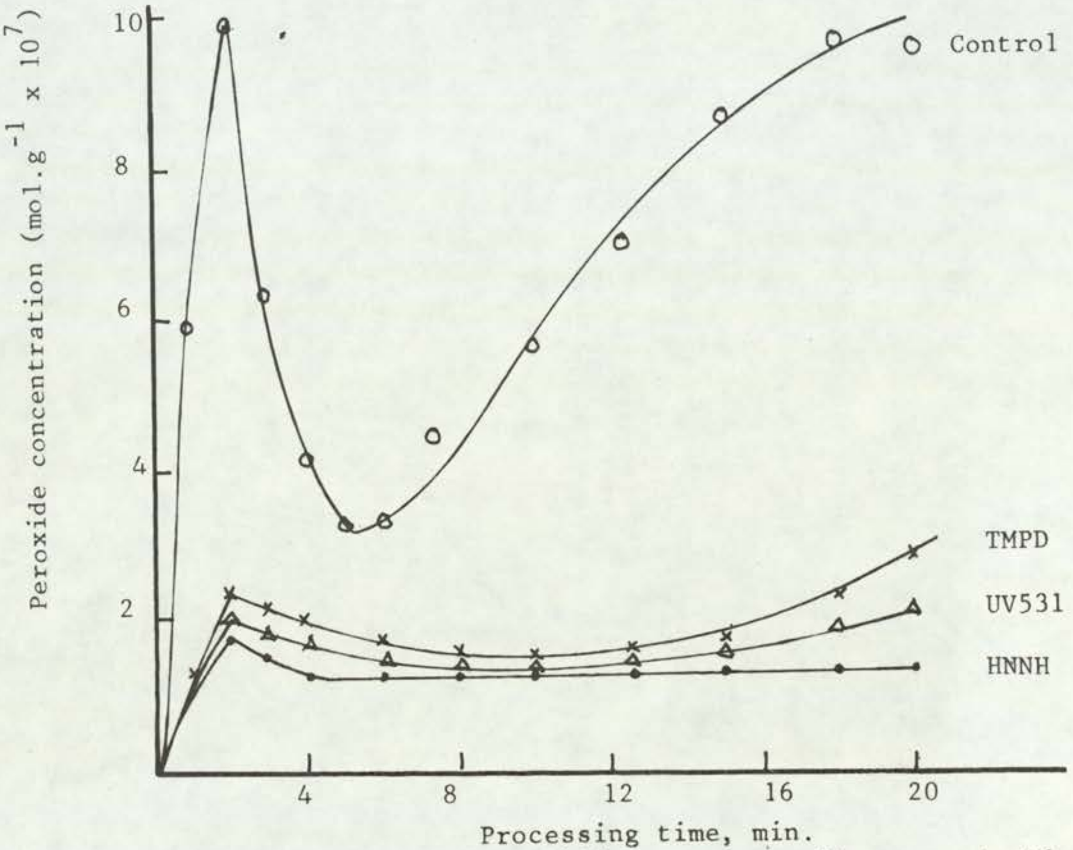


Fig. 5.29: Effect of stabilisers on peroxide concentration in PVC during irradiation. Formulations contain 2.9 x 10^{-3} mole % DBTM, 0.2 x 10^{-3} mole % uv stabilisers and lubricants.

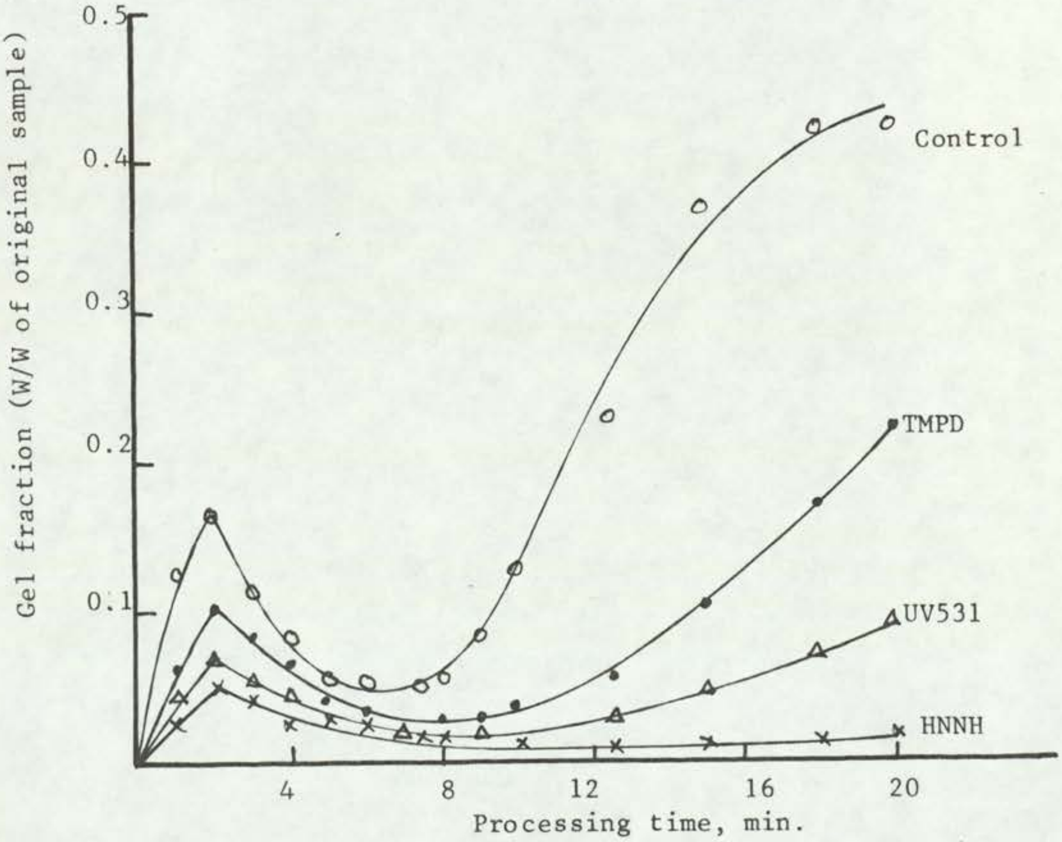


Fig. 5.30: Effect of stabilisers on gel formation in PVC during processing. (Formulations as in fig. 5.29)

This means that UV531 functions mainly as a uv screen for the polymer by absorption of the incident u.v. irradiation. Both TMPD and HNNH photostabilise by a different mechanism since hindered piperidines do not possess u.v.screening ability, nor do they quench triplet carbonyl or singlet oxygen[90,160]. The activity of hindered piperidines as uv stabilisers is primarily due to the formation of the derived nitroxyl radical which is an effective alkyl trap.[90,94]. This implies that both TMPD and HNNH stabilise the polymer by their radical trapping ability. UV531 was found to be more effective than TMPD but was less effective than HNNH (figs. 5.27-31).

Figure 5.32 shows the effect of TN and its esters, stearyl (SETN), Lauryl (LETN), oleayl (OETN) and propionyl (PETN) on carbonyl group index in PVC during uv irradiation. It is seen that the rate of photo-oxidation as measured by carbonyl formation is faster in the presence of the esters than in the tris nitro compound (TN) itself. This is consistent with the fact that lower times to embrittlement were obtained for samples stabilised with these esters than with TN (see table 5.1). This effect is probably due to a diluent effect of the ester chain on the effective nitro group. The Lauryl ester (LETN) was found to be the most effective of the esters used, while tris amine (TAM) was less effective than all the esters. The effect of these stabilisers on peroxide concentration during processing is shown in fig. 5.33. The stabilising activity of α-3,5-Dimethyl-4-hydroxylphenyl-N-isopropyl nitrone (IPN) in PVC was investigated but was found to be much less effective than both tris nitro and its esters. Consequently, work on IPN was terminated after preliminary investigation. Figure 5.34 shows a comparison of the activity of IPN with LETN and TN.

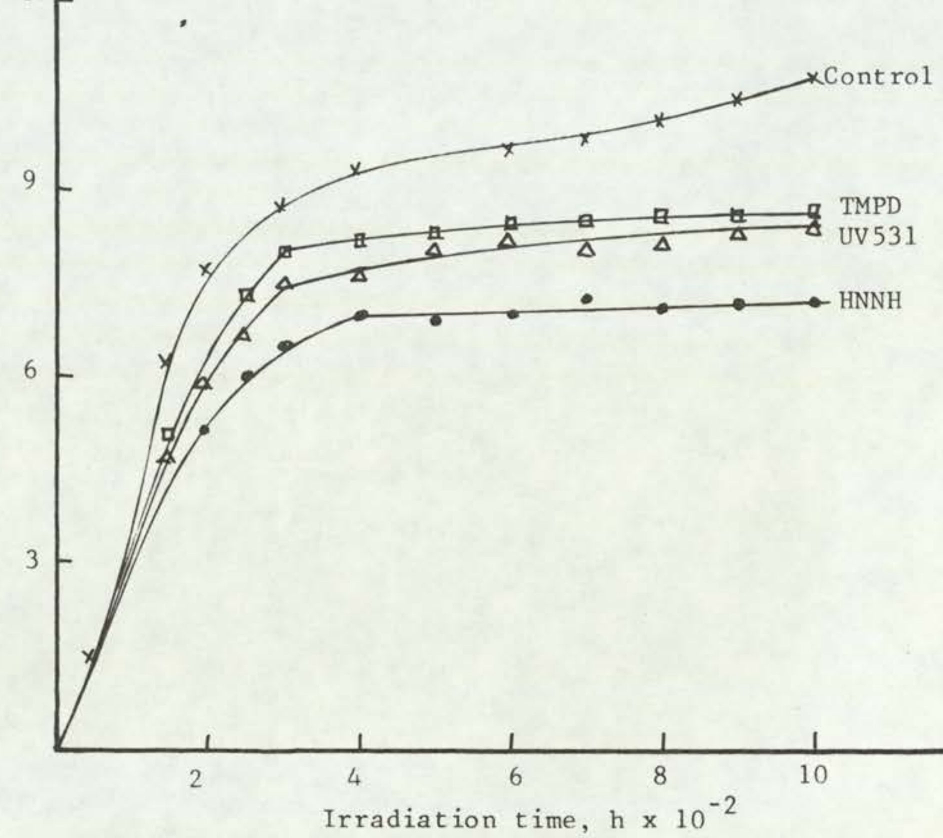


Fig. 5.31: Effect of stabilisers on carbonyl index in PVC during irradiation. formulations contain lubricants and DBTM/uv stabilisers (2.9/0.2) x 10^{-3} mole %.

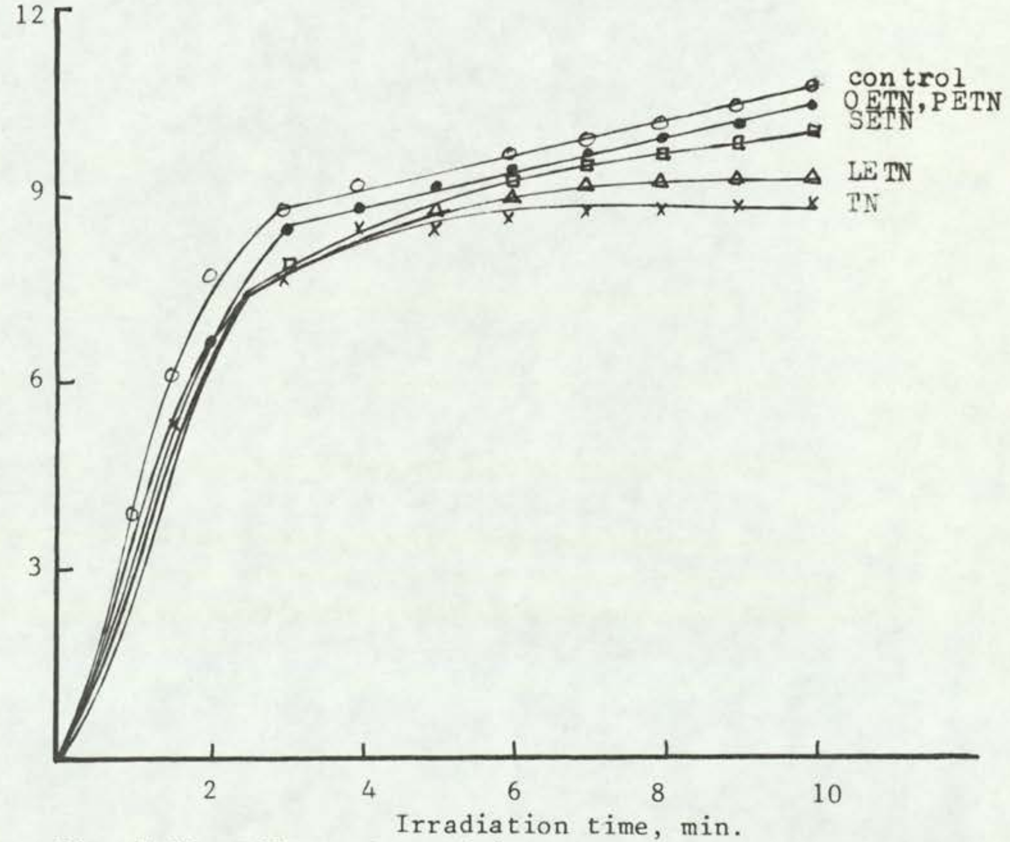


Fig. 5.32: Effect of stabilisers on carbonyl index in PVC during uv irradiation. Formulations as in fig. 5.31.

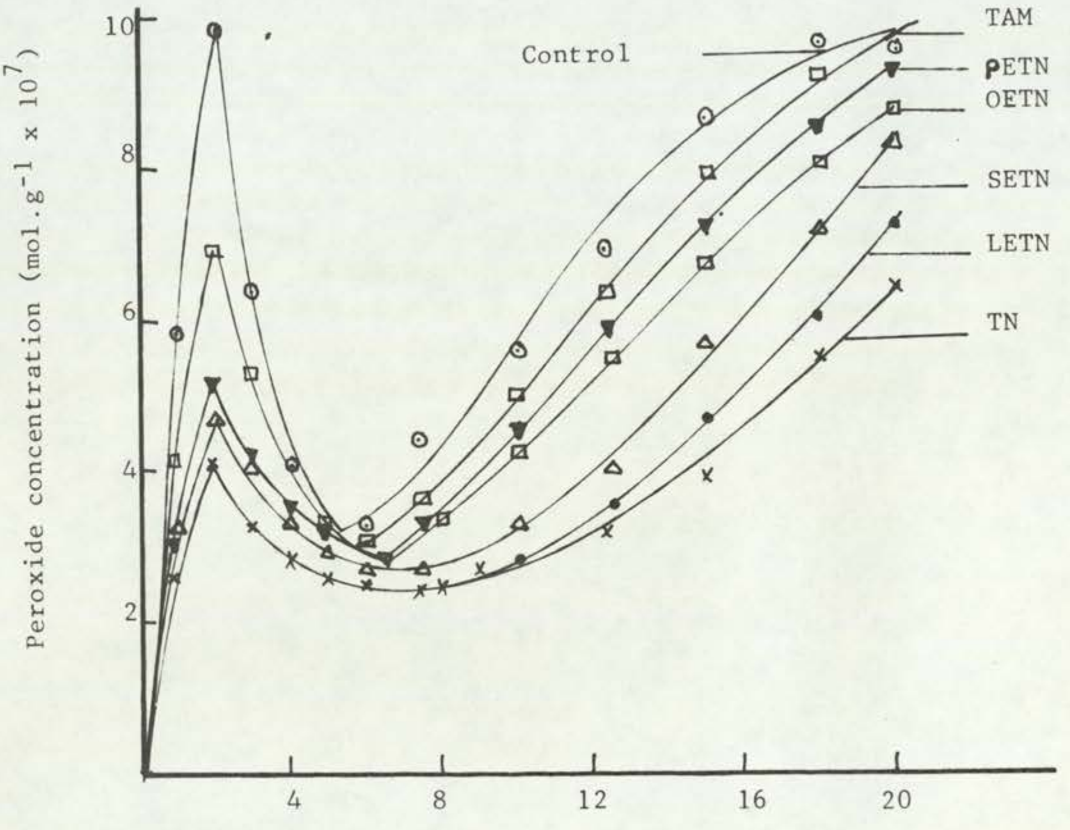


Fig. 5.33: Effect of stabilisers on peroxide concentration in PVC. Formulations contain (2.9 DBTM , 0.2 uv stabilisers) x 10^{-3} mole % and lubricants.

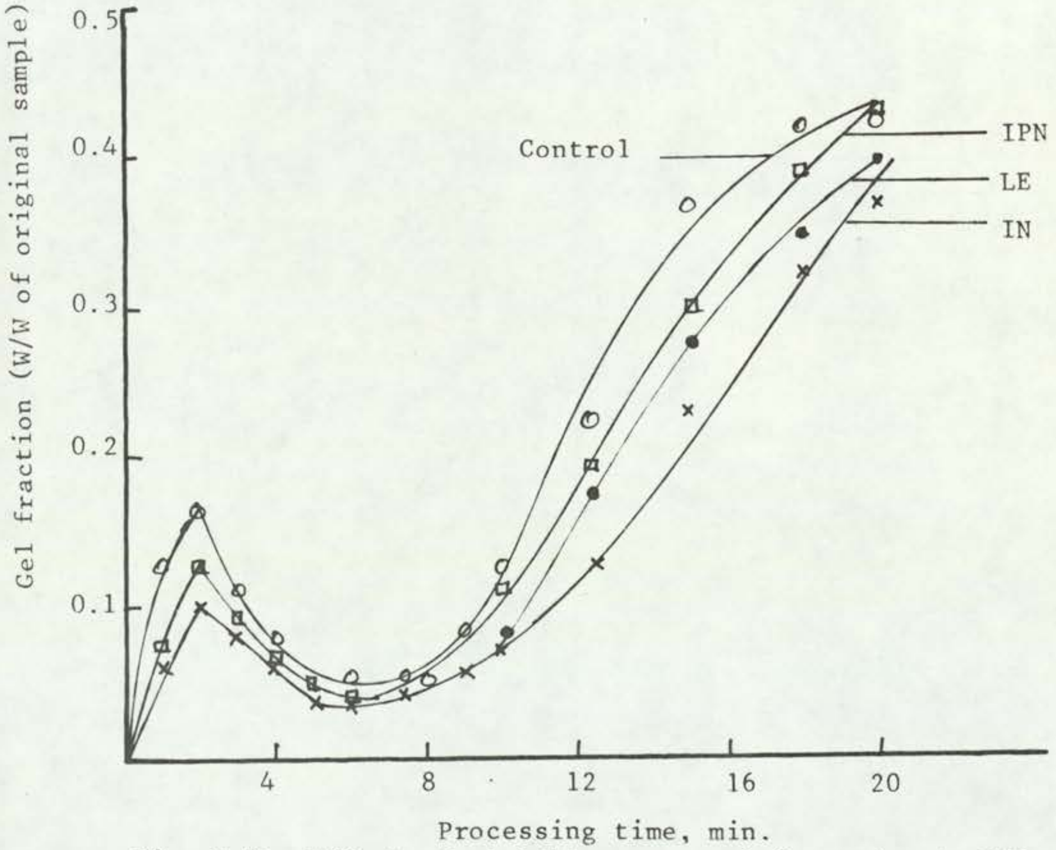


Fig. 5.34: Effect of stabilisers on gel formation in PVC
Captions as in fig. 5.33

Figure 5.35 shows the relation between the initial rate of thermal oxidation and the concentration of functional groups formed in PVC. This was done in order to relate what was found[135] during photo-oxidation to thermal oxidation. It was shown[135] that the rate of photo-initiation correlates well with initial peroxide concentration and that there is no correlation with unsaturation or carbonyl concentrations. This experiment was repeated and the results of fig. 5.36 confirm the earlier report[135] under photo-oxidative conditions while the results of fig. 5.35 show that a similar relationship exists under thermal oxidative conditions.

Studies in other polymers[139,161] have shown that the presence of minor amounts of initial unsaturation is a major cause of subsequent photo-oxidation as a result of allylic hydroperoxide formation. It is also known[162,163] that thermally produced peroxides in combination with unsaturation constitutes a powerful photo-initiating system. These findings demonstrate positively that the subsequent photo-stability of processed PVC is related to the concentration of hydroperoxides formed during the processing operation. The evidence presented in figs. 5.35 and 36 and previous reports[135,139,161-163] all confirm the key importance of hydroperoxides in all types of oxidative degradation processes and indicate that hydroperoxide decomposing mechanism occupy a central and critical position in the development and technology of polymer stabilisation.

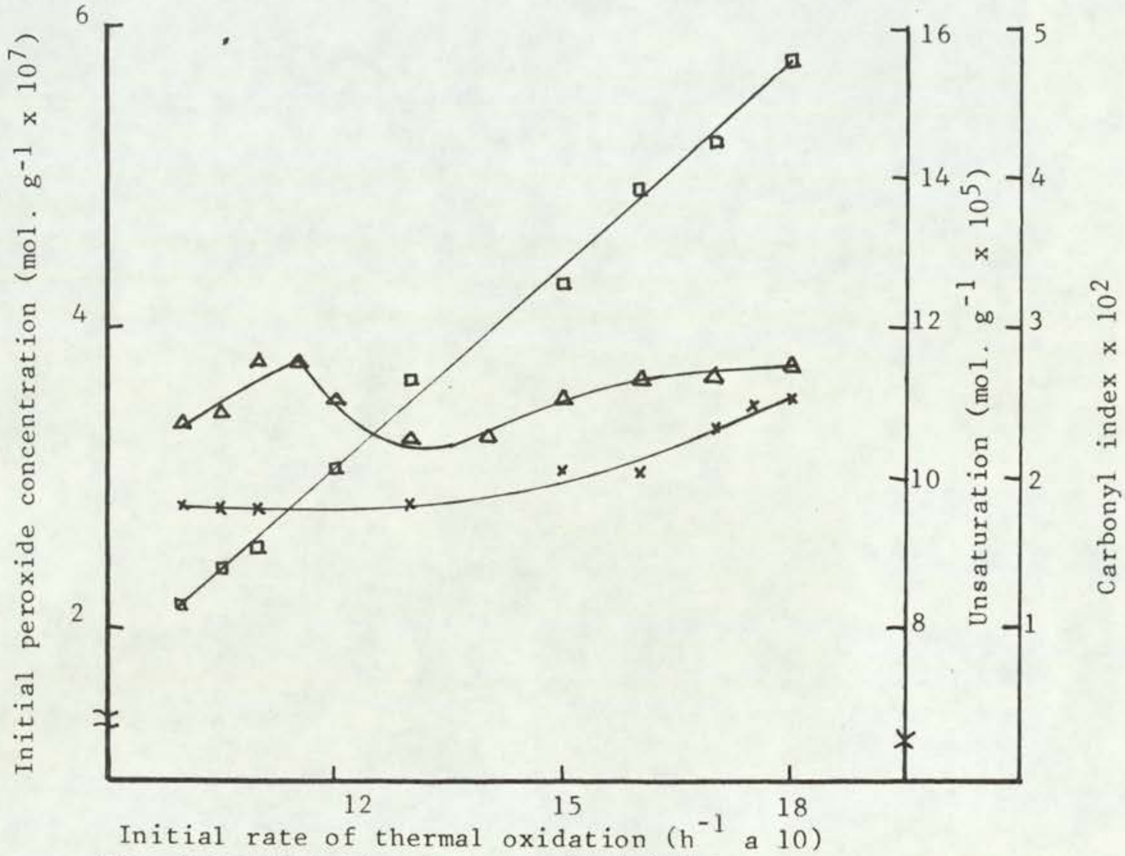


Fig. 5.35: Relation between the initial rate of thermal oxidation of PVC and the concentration of functional groups (a) peroxides; (b) carbonyl; (c) unsaturation.

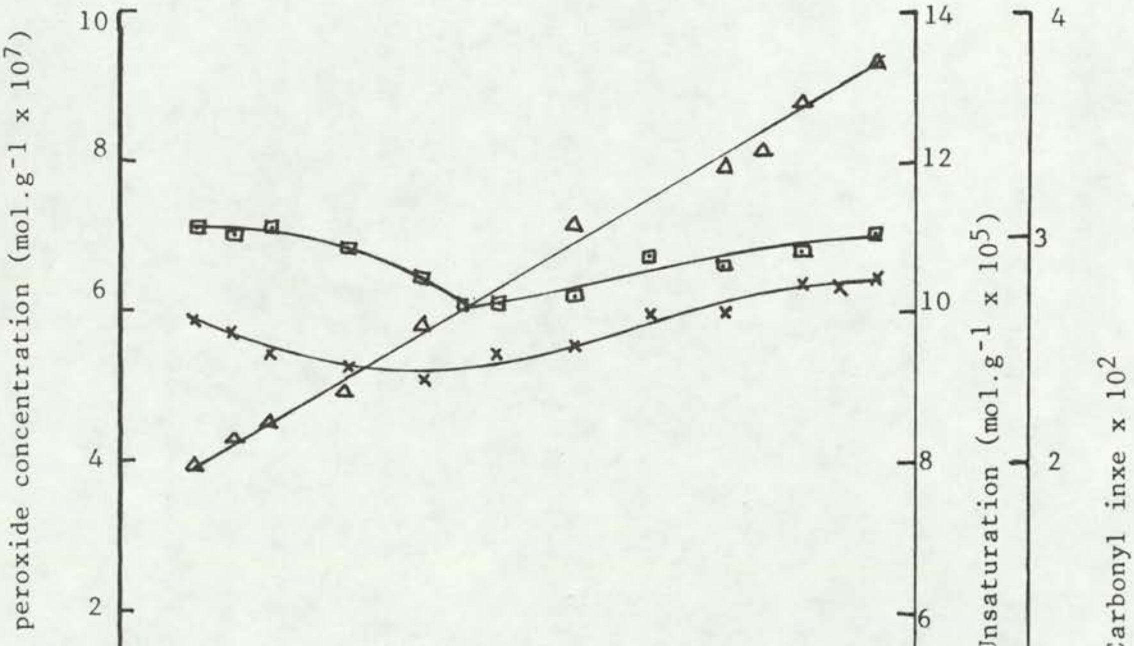


Fig. 5.36: Relation between the initial rate of photo-oxidation of PVC and the concentration of functional groups. (a) peroxides; (b) carbonyl index, (c) unsaturation.

5.3 The Role of Nitroxyl Radicals

The concentration of nitroxyl radicals in PVC samples stabilised with 2,2,6,6-tetramethyl piperidine (TMPD), its derived nitroxyl radical (TMPDO) and hydroxylamine (TMPDOH), bis (2,2,6,6-tetra methyl piperidinyl) sebacate (HNNH), its derived bis nitroxyl, (ONNO), and 2-methyl-2-nitrosopropane (MNSP) were measured by electron spin resonance JEOL-PE, spectrometer (Chapter 2). One purpose of this study is to understand the mechanism of action of the photostabilisers. All the formulations reported here also contain 7.2×10^{-3} mole % DBTM as the basic melt stabiliser of PVC during the processing operation.

The variation of nitroxyl concentration with time of processing in samples stabilised with DBTM/TMPD is shown in fig. 5.37. Each bar on the curves shows the spread of results for 4 experiments. It is found that the nitroxyl concentration goes through a sequence of decay followed by growth until after 24 min when a minimum equilibrium concentration was reached. This behaviour closely resembles the variation of nitroxyl concentration observed in polypropylene during processing at 180-200°C in a closed mixer[164] or of galvinoxyl under similar conditions[96,165], and has been explained on the basis of the simultaneous variation of both shear and oxygen concentration in the mixer[96,108,165,166]. A similar behaviour has also been reported recently in rubber.[167]

Figure 5.38 shows that a similar alternating decay and growth in concentration occurs in the presence of HNNH. The monofunctional

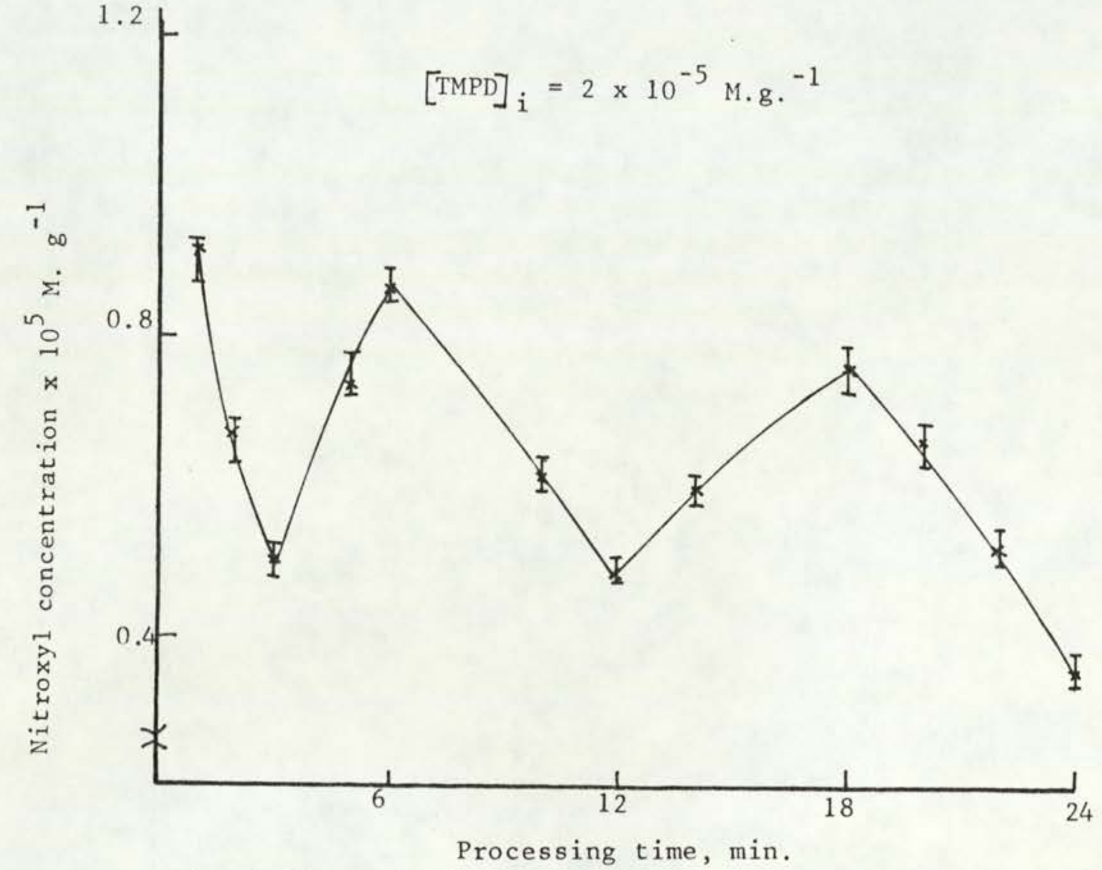


Fig. 5.37: Variation of nitroxyl concentration with time of processing at 180°C. Formulation contains 7.2×10^{-3}M DBTM as the basic melt stabiliser and lubricants

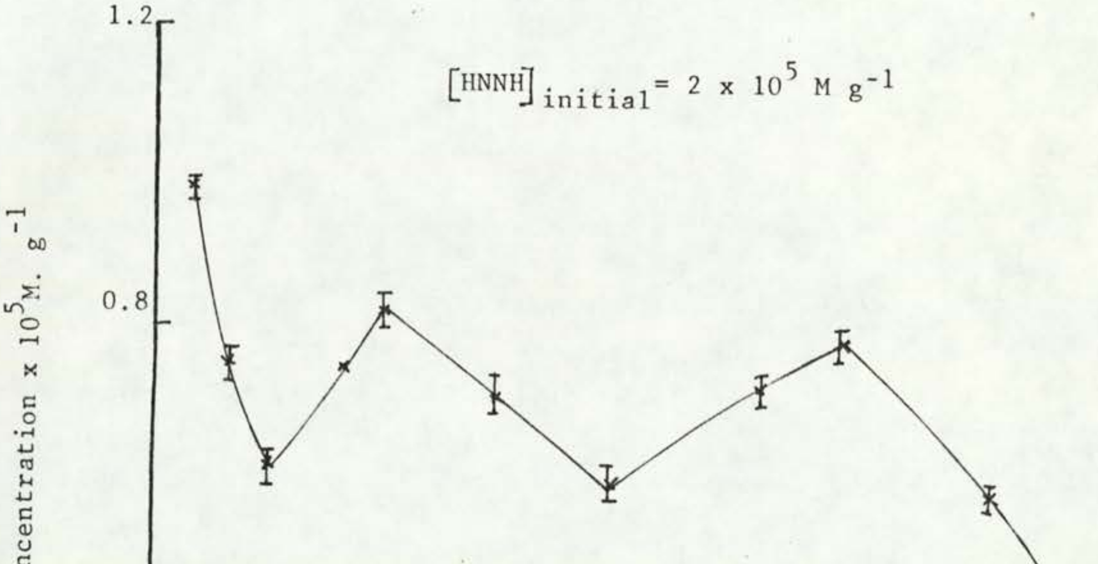


Fig. 5.38: Variation of nitroxyl radical with time of processing at 180°C. Formulation as in fig. 5.37

nitroxyl (TMPDO) and the bisnitroxyl (ONNO) also undergo the same alternating sequence suggesting that the nitroxyl is first reduced and subsequently regenerated from the reduced derivative. The similarity between the stabilising activities of TMPD and TMPDO; and between HNNH and ONNO agrees with the effects of these stabilisers on functional groups (see figs. 5.21-24) and shows that these stabilisers act by similar mechanisms. This also suggests that the parent amines are oxidised to the nitroxyl radicals during processing (figs. 5.37-40).

Nitroxyl radicals were also detected in PVC samples stabilised with MNSP although in this case, the alternating sequence which was observed in the case of TMPD, TMPDO, TMPDOH, HNNH and ONNO could not be established. However, nitroxyl concentration was found to increase with increase in the initial concentration of MNSP incorporated into the polymer (fig. 5.41). A similar effect was obtained in the presence of N-phenyl and N-methyl nitrones as shown in fig. 5.42. At the same molar concentration of MNSP, the concentration of the derived nitroxyl radical was found to decrease with increasing processing time (fig. 5.43).

Tables 5.1-3 show the u.v. embrittlement of PVC samples formulated with DBTM and photostabilisers.

5.4 **Discussion**

The formation of nitroxyl radical from the nitroso compound (MNSP) may be explained in terms of the trapping of the initially formed

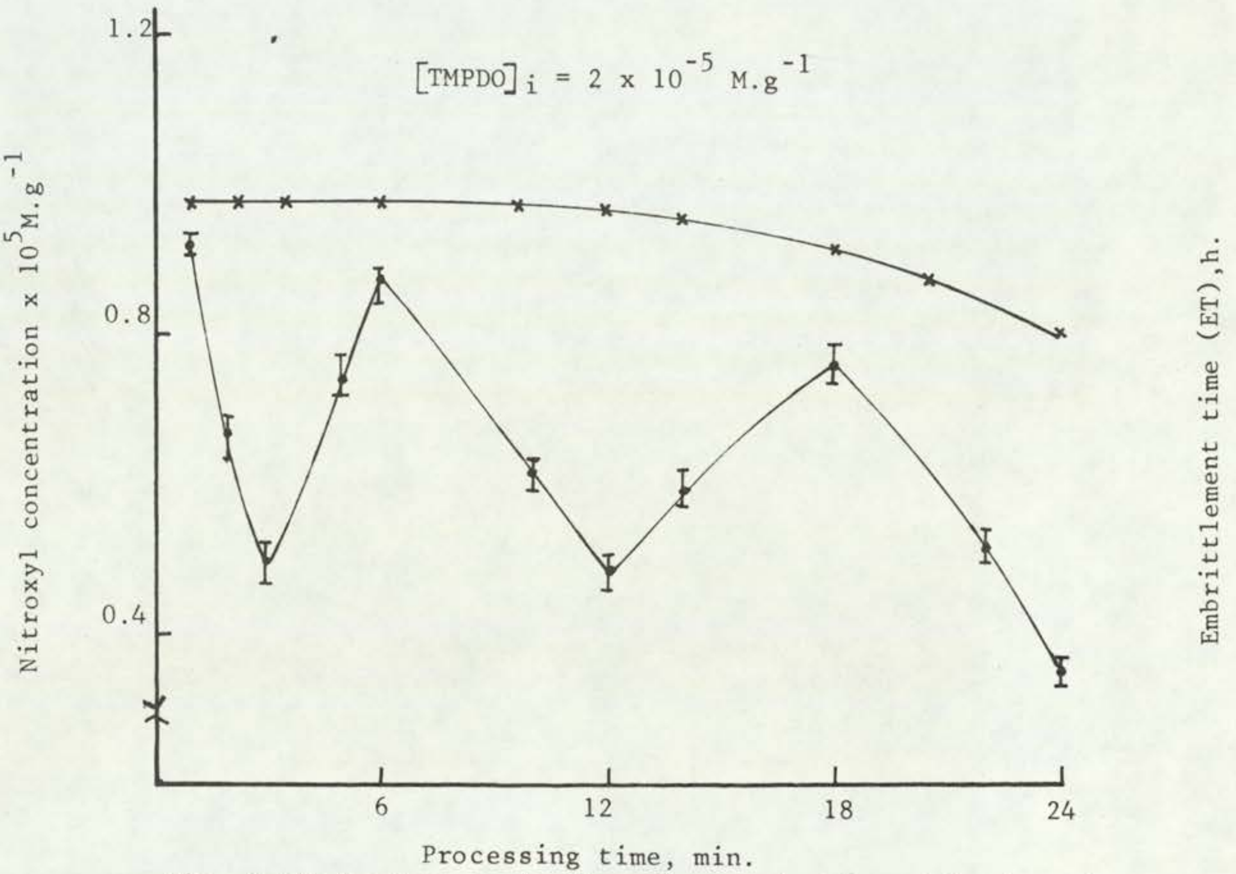


Fig. 5.39: Variation of nitroxyl cocentration with time of processing at 180°C and the changes in embrittlement time. Formulation contains 7.2×10^{-3} M DBTM and lubricants.

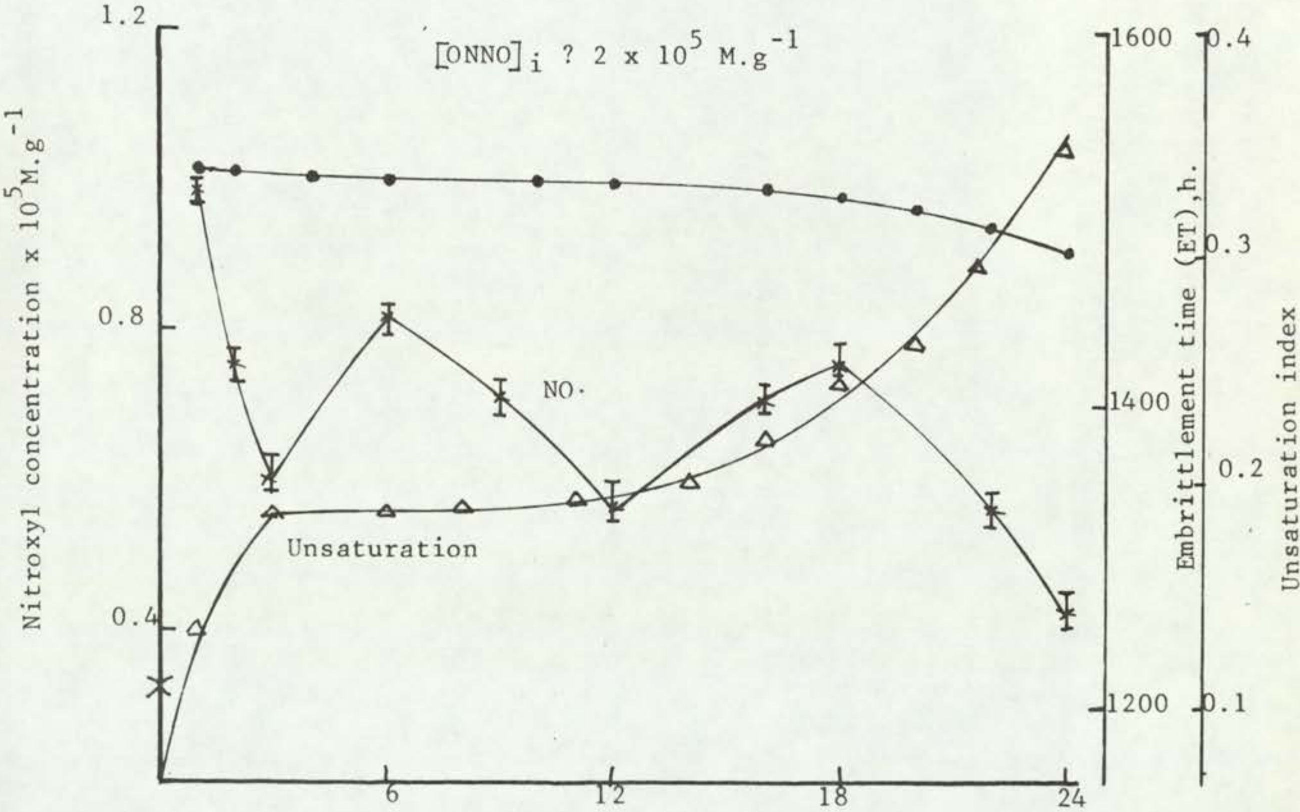


Fig. 5.40: Variation of nitroxyl concentration with time of processing at 180°C and the changes in unsaturation and embrittlement time. Formulation contains 7.2×10^{-3}M DBTM and lubricants.

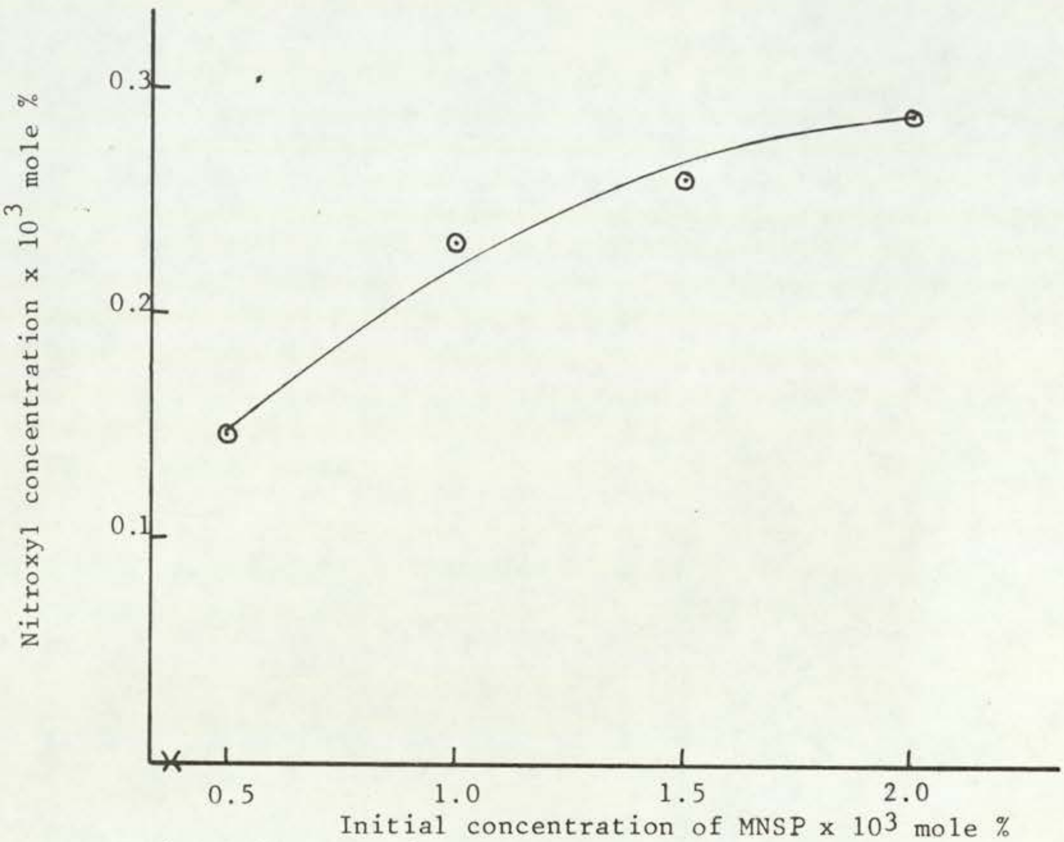


Fig. 5.41: Relation between initial concentration of MNSP and nitroxyl concentration. Samples processed at 180°C for 6 min. in the presence of lubricants and 7.2×10^{-3} mole % DBTM.

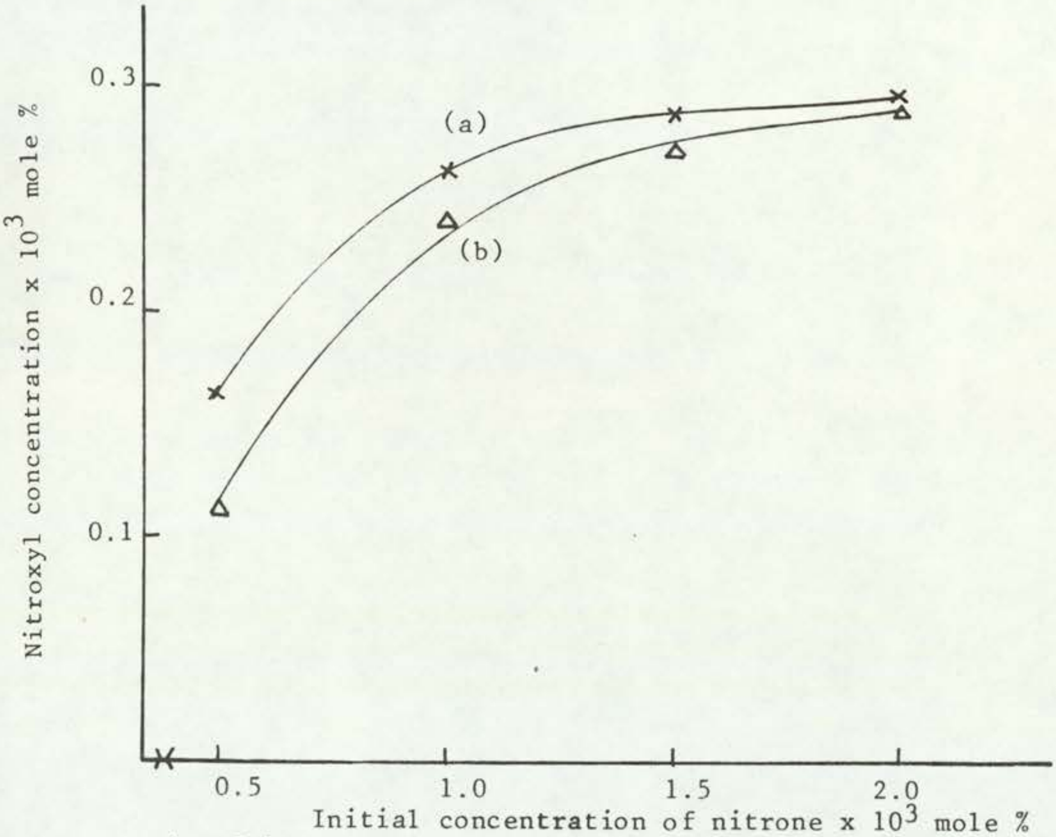


Fig. 5.42: Relation between initial concentration of nitrone and the derived nitroxyl radical. Formulation as in fig. 5.41

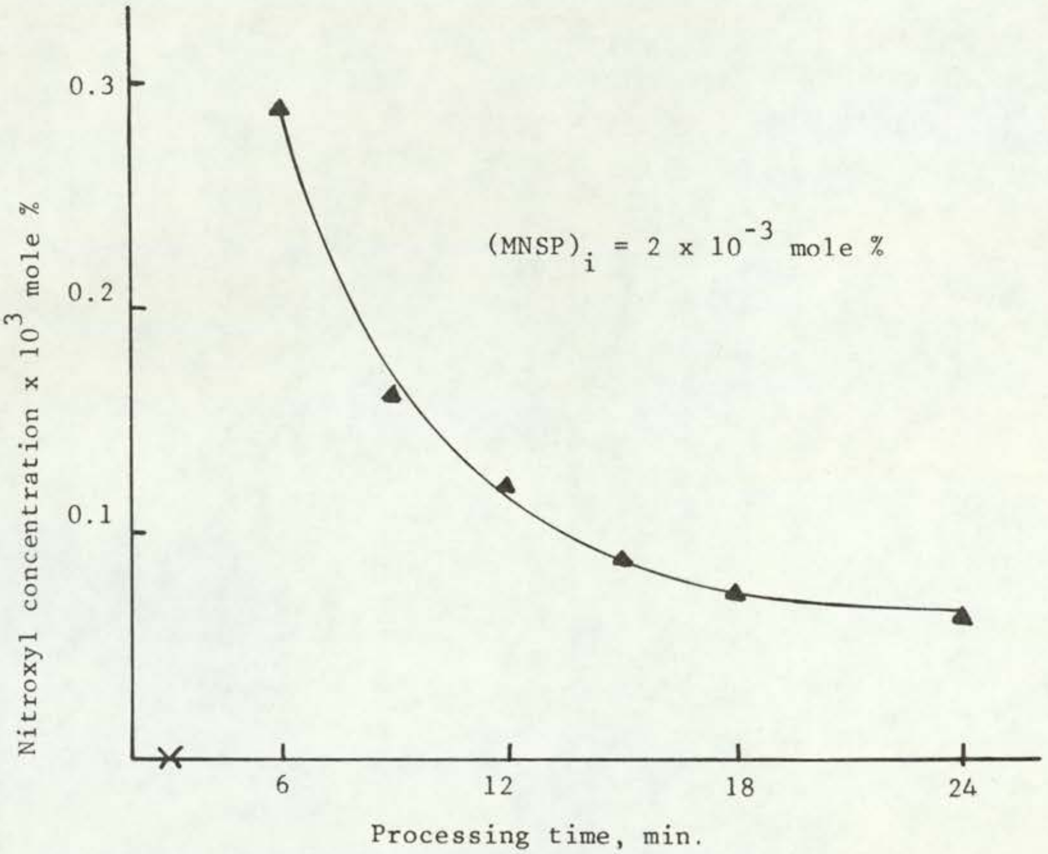


Fig. 5.43: Variation of nitroxyl concentration with processing time at 180°C. Samples contain lubricants and 7.2×10^{-3} mole % DBTM.

TABLE 5.1

UV Embrittlement Time (hr) of DBTM Synergists with other additives

Processing Time (min)	Basic Additive	UV531 0.25g%	Tin 770 0.25%	MNSP 0.25g%	DBTM Alone	CONTROL
5	2g% DBTM	1256	1352	1182	950	658
10	"	1248	1321	1144	920	600
15	"	1166	1228	1096	870	537
20	"	1120	1160	1055	844	562
5	2.5%DBTM	1372	1448	1250	986	
10	"	1368	1432	1246	972	
15	"	1280	1374	1188	925	
20	"	1192	1269	1133	925	

TABLE 5.2

UV Embrittlement time (hr)

Effect of concentration on UV stability of Synergistic Combinations of DBTM with other Additives - All Samples were processed for 5 min at 180°C

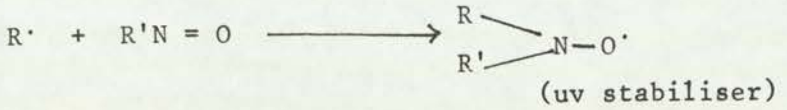
Synergist	2g% DBTM Concentration x 10^{-4} M				2.5g% DBTM Concentration x 10^{-4} M			
	1	2	5	10	1	2	5	10
UV531	1168	1224	1256	1288	1182	1250	1372	1404
Tin 770	1242	1325	1352	1366	1260	1390	1448	1482
ONNO	1260	1292	1368	1388	1286	1377	1464	1508
TMPD	1144	1260	1338	1350	1156	1288	1408	1420
TMPDO	1180	1272	1344	1355	1212	1324	1422	1436
TMPDOH	1190	1284	1352	1360	1220	1324	1430	1444
MNSP	1084	1122	1182	1240	1096	1152	1250	1260
TN	1138	1166	1204	1280	1152	1168	1268	1283
TAM	1048	1102	1162	1225	1050	1115	1176	1184
LETN	1106	1152	1188	1244	1138	1154	1250	1268
SETN	1068	1128	1175	1231	1068	1130	1192	1244
OETN	1056	1113	1168	1228	1077	1122	1180	1232
PETN	1052	1106	1164	1225	1064	1117	1178	1228
IPN	1000	1038	1086	1108	1036	1068	1120	1155

TABLE 5.3

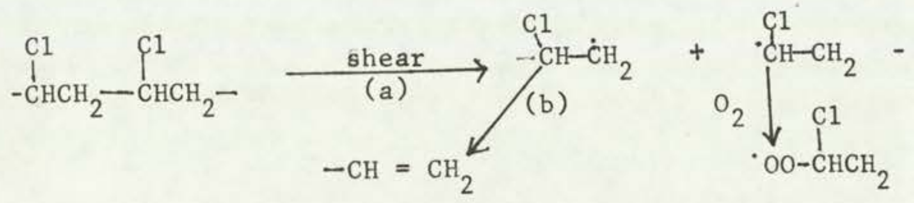
UV Embrittlement Time (hr) of PVC Formulations

Synergistic Combinations (1:1; 0.5g%)	DBTM, 2g% $(5.77 \times 10^{-3} M)$%					DBTM, 2.5g% $(7.2 \times 10^{-3} M)$%					Comments on Colour of Processed Samples
	Processing Time (Min)					Processing Time (Min)					
	2	5	10	15	20	2	5	10	15	20	
UV531+Tin 770	1640	1656	1684	1622	1468	1664	1787	1792	1668	1525	White, clear
UV531+ONNO	1766	1770	1725	1686	1553	1770	1783	1732	1690	1550	Bright yellow colouration in films
UV531+TMPD	1588	1595	1620	1577	1421	1592	1618	1634	1590	1445	Clear
UV531+TMPDO	1608	1610	1592	1544	1473	1615	1633	1606	1570	1493	Bright yellow Colouration
UV531+TMPDOH	1600	1622	1602	1558	1490	1611	1640	1612	1573	1502	Clear
UV531+ MNSP	1458	1535	1502	1320	1284	1477	1579	1528	1355	1300	Blue/Green Colour
UV531+ DPNO	1384	1406	1375	1296	1265	1416	1462	1454	1325	1284	
UV531+ TN	1468	1520	1508	1360	1295	1484	1533	1526	1388	1307	Opaque, Ash colour on exposure
UV531+ TAM	1355	1328	1278	1252	1239	1370	1360	1302	1276	1255	Opaque, ash-colour on exposure
Tin 770+TN	1472	1518	1513	1368	1290	1488	1532	1528	1384	1333	"
Tin 770+ TAM	1349	1350	1270	1246	1235	1364	1375	1294	1268	1246	"
Tin 770+ MNSP	1462	1518	1494	1338	1268	1479	1564	1522	1466	1328	Greenish Colouration
Tin 770+DPNO	1396	1484	1408	1312	1277	1448	1525	1476	1337	1292	
Control	630	658	600	537	562	–	–	–	–	–	

alkyl radicals, produced by mechanodegradation (4), which eliminates or reduces the subsequent loss of hydrogen chloride (5 step b).

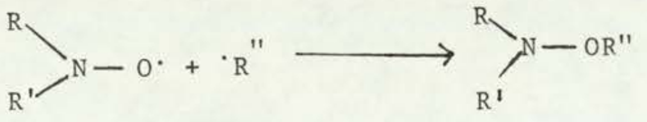


(4)



(5)

It is expected that the resulting nitroxyl radical of reaction (4) will combine with more alkyl radicals in the system according to equation (6)



(6)

Evidence for the foration of the nitroxyl radical was obtained from the esr spectroscopy while evidence for the formation of the substituted alkyl hydroxylamine of reaction (6) was obtained from gel permeation chromatrography. Figure 5.44 demonstrates clearly that the presence of MNSP leads to the formation of high molecular weight species in the processed sample compared to the control without additives.

The ratios $\overline{Mw}/\overline{Mn}$ and $\overline{Mz}/\overline{Mn}$ are measures of high molecular weight species present in any heterogenous polymer system. Moreover, the latter ratio ($\overline{Mz}/\overline{Mn}$) may be used as a measure of crosslinking in the polymer. Table 5.4 shows the data of these ratios obtained in PVC samples processed with and without MNSP. It is evident that the presence of MNSP caused a substantial increase in both $\overline{Mw}/\overline{Mn}$ and $\overline{Mz}/\overline{Mn}$ compared with DBTM; the small values obtained in the presence of DBTM are consistent with the fact that as an effective melt stabiliser for PVC, both chain scission and crosslinking processes are reduced by this stabiliser.

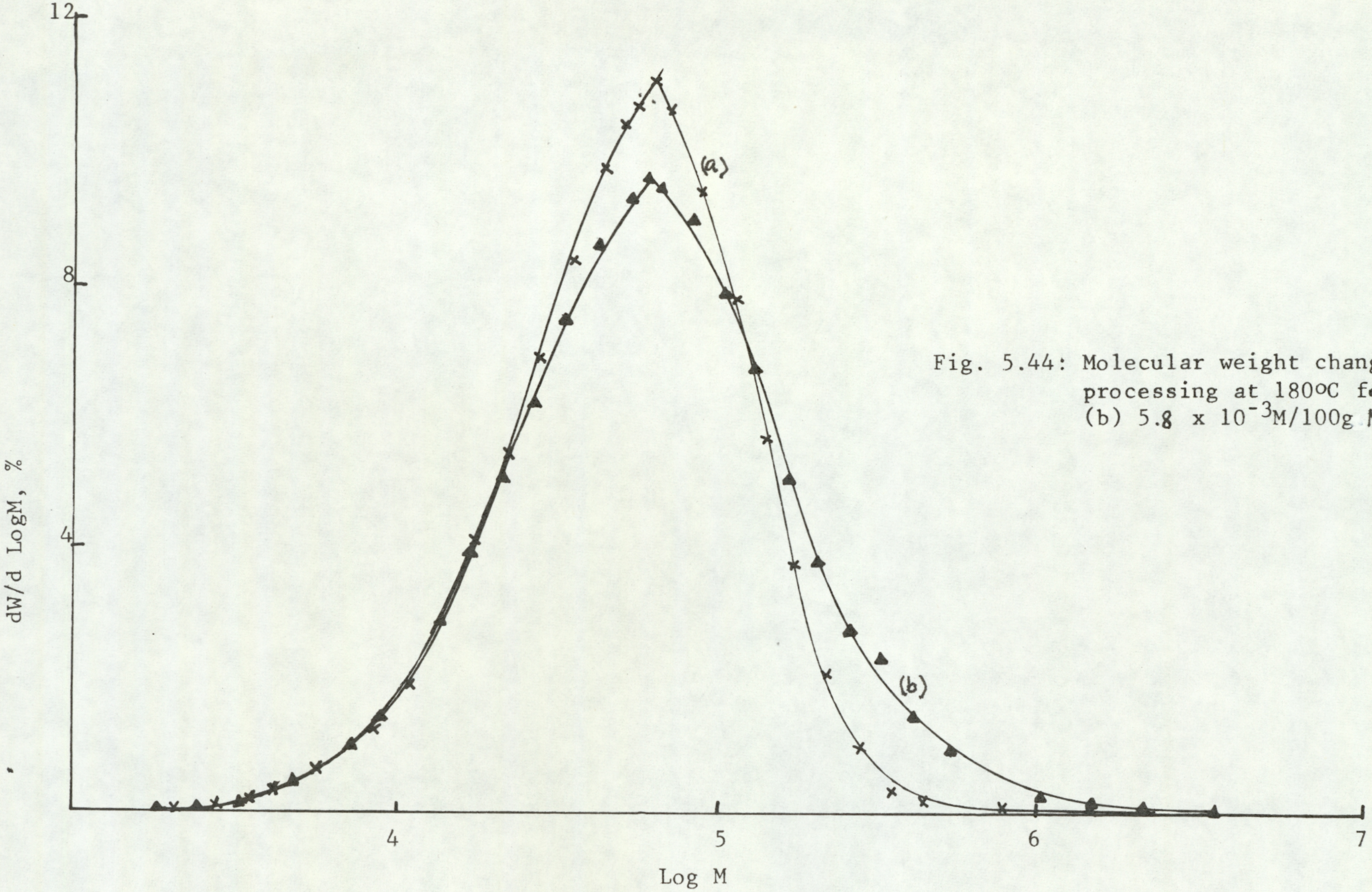


Fig. 5.44: Molecular weight changes in PVC during processing at 180°C for 5min. (a) Control; (b) 5.8 x 10^{-3}M/100g MNSP

Table 5.4 Molecular weight parameters of PVC with stabilisers

Processing Time (min)	Stabiliser 10^{-3}mole %	Mw/Mn	Mz/Mn
0	-	2.4	6.11
5	-	2.92	10.40
10	-	4.37	27.60
15	-	4.39	29.54
20	-	5.29	36.80
5	MNSP (2.0)	2.73	7.29
10	MNSP (2.0)	5.05	44.26
20	Lubricants	2.66	6.25
20	DBTM + Lubricants	3.10	21.02
20	DBTM/MNSP: (7.2/2)	8.10	107.54
5	DBTM (7.2)	2.26	3.95
10	"	2.49	5.23
15	"	2.94	7.78

There is almost universal agreement that the activity of hindered piperidines as uv stabilisers is primarily due to the formation of the derived nitroxyl radical which is an effective alkyl radical trap[90,94].Studies in polypropylene have shown that the resulting alkylhydroxylamines are photounstable[166] and dissociate followed by disproportionation to olefin and free hydroxylamines. This in turn is readily reoxidised by alkylperoxyl radical in a CB-D process to regenerate the nitroxyl radical which then repeats the cycle.

In the present work, it was difficult to relate the formation of unsaturation to the presence of nitroxyl radical or the parent amine in that DBTM was always used in combination with the uv stabilisers. When PVC was processed in the presence of the photostabilisers alone, the discolouration formed in the stabilised samples was very similar to that formed in the control sample without additives such that the technological evaluation of the stabilisers alone could not be made with a reasonable degree of reproducibility. It is significant to mention that a similar observation was made with other compounds. During the preliminary stage of this work, the phenolic antioxidants Irg.1300, 1076 and 1010, N-phenyl and N-methyl nitrones, MNSP, UV531, HNNH and several other commercial phenolic antioxidants were processed alone with PVC at 180°C. In all cases, the polymer became extensively discoloured after only a short processing time (3-5 min) demonstrating the ineffectiveness of these compounds to stabilise PVC against colouration when used alone. This evidence emphasises the important and primary role of the metal component of any thermal stabiliser for PVC in reacting with hydrogen chloride.

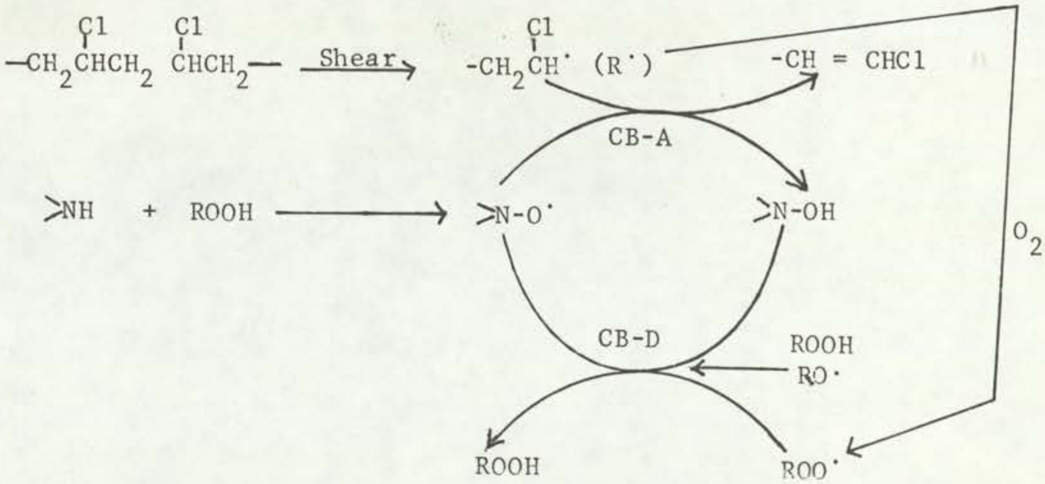
Although hindered piperidines are not catalysts for the destruction of hydroperoxides, they react with hydroperoxides in a stoichiometric reaction during the processing of polyolefins giving the corresponding nitroxyl radicals[168] (7). Once formed, the hindered nixtroxyl radicals

$$>N-H + ROCH \longrightarrow >N-\dot{O} + H_2O + RO^{\cdot} \qquad (7)$$

are effective macroalkyl radical traps[169-17]. An alternative regenerative mechanism was proposed for thermal and mechanochemical stabilisation of polypropylene in which hydroxylamines act as reservoirs for the nitroxyl and the exceptional efficiency of the regenerative mechanism results from the participation of the complementary chain-breaking donor (CB-D) and chain-breaking acceptor (CB-A) antioxidant mechanism[173]. Further work which support this cyclic regeneration mechanism have been reported recently[164-167].

The present results may also be rationalised by a similar cyclic regenerative mechanism (Scheme 5.1)

Scheme 5.1. Stabilisation of PVC by Hindered Amines



([$>NOH + ROOH \longrightarrow H_2O + RO^{\cdot} + >NO^{\cdot}$]); Provided there is an excess of alkyl radicals in the system, i.e. under high rate of initiation and limited oxygen access, inhibition will predominate).

The oxidation of the parent amines to nitroxyl radicals in PVC may occur readily by reaction (7) since hydroperoxides are formed rapidly during the first minutes of processing of unstabilised PVC[67] and its concentration is not reduced completely to zero in the presence of DBTM/piperidines (2.9/0.2 x10^{-3} mole %) as may be seen in figure 5.21.

The hindered piperidines and their derivatives have been found to be better melt stabilisers than nitroso propane, MNSP. The superior activities of piperidines over MNSP may be explained in terms of the cyclic regenerative mechanism (figs. 5.37-40) which was found to be absent in the case of MNSP (fig. 5.43). Hindered piperidine compounds are known to be converted rapidly to the corr~~r~~esponding nitroxyl radicals under oxidising conditions[159] which include commercial processing operations[90]. The nitroxyl radical is formed in a stoichiometric reaction from the parent amine and the subsequent exceptional efficiency of the regenerative mechanism results from the participation of the complementary chain-breaking donor (CB-D) and chain-breaking acceptor (CB-A) antioxidant mechanisms[161] involving the derived nitroxyl radical and hydroxylamine. The hydroxylamine is readily reoxidised by alkylperoxyl radical in a CB-D process to regenerate the nitroxyl radical which traps alkyl radicals. In this way, antioxidant reactions remove both alkyl and alkylperoxyl radicals from the autoxidising system and leads to the continuous regeneration of the nitroxyl radical until it is finally depleted by non-stabilising side reactions.

The photostabilising activities of the hindered piperidine compounds TMPD, TNPDO, TMPDOH, HNNH and ONNO may similarly be rationalised on the basis of the cyclic regenerative mechanism and the removal of both alkyl and alkylperoxyl radicals discussed above.

CHAPTER SIX

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 CONCLUSIONS

Mechanical shearing of the polymer chains during processing is the main source of chemical impurities in PVC by the incorporation of hydroperoxides and olefinic unsaturation into the polymer; species which reduce both the thermal and photo-oxidative stability of PVC. Mechanochemical degradation during the processing operation involves competing chain scission and crosslinking reactions such that the number average molecular weight, $\overline{M}n$, of PVC samples remains essentially unchanged. On the other hand, appreciable changes occur in the values of the viscosity, weight and Z-average molecular weights of the polymer during processing.

Wax E, a commercial ester lubricant and Calcium stearate reduced the severity of the mechanochemical damage inflicted on the polymer during processing. The formation of both unsaturation and hydroperoxides was delayed by Dibutyltin maleate (DBTM) which not only reacts with allylic chlorine and hydrogen chloride but also undergoes Diels Alder addition to conjugated unsaturation. Lead stearate gives comparable melt stability to PVC but is less effective than DBTM under thermal and photo-oxidative conditions.

The thermal oxidative stability of PVC samples stabilised with DBTM is synergistically improved by the additional presence of phenolic antioxidants Irganox 1300, 1076 and 1010. The activities of these phenolic antioxidants are found to be directly related to their molecular weights, indicating that antioxidant activity is related to molecular weight and volatility under thermal oxidative conditions in a flow of air.

Hydroperoxides and unsaturation formed during processing initiate the polymer to photo-oxidation and both DBTM and PbSt which reduce the concentrations of these species during thermal processing also exhibit some photostabilising activities during u.v. exposure.

Hindered piperidines and their derived nitroxyl radical and hydroxylamine function as photostabilisers for PVC through a cyclic regenerative mechanism which result from the participation of the complementary chain-breaking donor (CB-D) and chain-breaking acceptor (CB-A) antioxidant mechanisms. Nitroxyl radicals are also formed in PVC samples stabilised with MNSP although no evidence for cyclic regeneration is found.

Tris amine (TAM), tris nitro (TN) and its stearyl, lauryl, oleayl and propionyl esters, diphenyl nitrones and α-phenyl-N-methyl nitrones all function as photostabilisers for PVC but they are less effective than the hindered piperidines.

The initial rates of thermal and photo-oxidation correlate well with hydroperoxide concentration demonstrating the key importance of peroxides in all oxidative degradation processes and consequently, emphasising the relevance of peroxide decomposers in the stabilisation technology of PVC both during processing and in service.

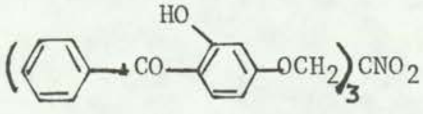
6.1.2 Suggestions for Further Research

Although organotin compounds are very effective stabilisers for PVC, they are rather expensive. This is a limitation to their industrial applications in terms of cost-effectiveness and profitability. The problem of toxicity is also of concern to health and the enviroment. Therefore, the search for suitable alternatives to the tin-based stabilisers currently in wide use constitutes a viable objective.

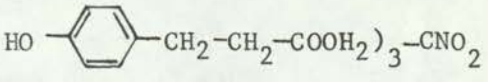
Synergistic combinations of metal stabilisers based on calcium/zinc and barium/cadmium carboxylates with epoxy compounds which are capable of reacting with HCl and with allylic chlorine may be investigated.

The effect of barium/cadmium carboxylates in combinations with phosphites may also be investigated.

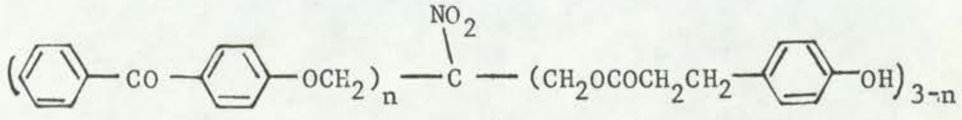
It is anticipated that the activity of Tris Nitro (TN) may be improved considerably by the incorporation of synergistic groups into the molecule. This may be particularly beneficial since there are three reactive hydroxyl groups in tris nitro which permit variation of the number of antioxidant functions per molecule of the derived products. Compounds I and II, and possibly III may be synthesised and tested as synergists with metal carboxylates.



I



II



III (**n=1** or 2)

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