The development of silicone sponge by using a non-toxic blowing agent

Caroline Pillon

A thesis submitted for the degree of

Master of philosophy

Aston University
September 2005

"This copy of the thesis has been supplied on condition that anyone who consults it is understood to recognise that its copyright rests with its author and that no quotation from the thesis and no information derived from it my be published without proper acknowledgement."

Aims of the project

The aims of the project are:
- The development and implementation of a suitable process for the manufacture of closed-cell sponge- formed silicone rubber, through the identification and validation of a suitable non-toxic blowing agent;
- The establishment of a curing process compatible with the chosen blowing agent; the definition of formulation for a range of grades of silicone rubber;
- The application of the formulation, blowing agent and curing process to the production for commercial sales.

The goals of the project have been established by the company in collaboration with Knowledge Transfer Partnerships (KTP) and Aston University.
KTP is a UK organisation, which helps companies to develop or to grow new business by offering them a government grant (around £94,000) and the support of an UK University. A graduate is employed to do a particular project (two years program). There are benefits for the company, the University and the graduate, such as new business, new contacts, possibility to do higher degree etc. David Britton was the person in charge from KTP on this project.

The project was performed in Primasil Silicones Ltd, Hereford. This company was formed in 1978. Primasil Silicones Ltd is a SME and employs around 88 people. This company manufactures silicone products and produces silicone compounds.

Aston University

The development of silicone sponge by using a non-toxic blowing agent

A thesis submitted for the degree of Master of Philosophy by

Caroline Pillon
September 2005

SUMMARY

Silicone sponges are silicone rubber with cell structure and are produced by adding a chemical blowing agent to the formulation. The main blowing agents used are 2,2-azobisisobutyronitrile, azodicarbomide (ADCA) and dinitrosopentamethylenetetramine (DPT) but all are producing toxic by-products. The silicone industry is looking for non-toxic blowing agent.
Primasil has already a formulation to produce sponges but the properties of their sponges and the consistence of its cell structure are limited by different factors such as the conditions of the cure and the type of blowing agent which is baking powder. Primasil sponges have a high density, small shape, and open-cells and non-uniform structure.

The aim of this project was to develop and to implement a suitable process for the manufacture of closed-cell sponge formed silicone rubber through the identification and validation of a suitable non-toxic blowing agent; to establish a curing process compatible with the chosen blowing agent; to define a formulation for a range of grades of silicone rubber and finally to apply the formulation, blowing agent and curing process to the production for commercial sales.

A literature research and some observations were done on the Primasil formulation, on the suppliers of sponges and on the current blowing agents sold. The elimination of blowing agents and methods of processing before conducting some trials was based on several parameters: safety of operators, protection of the environment and properties of blowing agent. From there, different blowing agents were tried with two established methods (c.f. part 9) in order to produce some silicone sponges by utilising a non-toxic chemical. First, efforts were focused on acquiring a new formulation and a suitable process for it. When formulations and process were defined, the work was concentrated on the properties of the product such as density, cell structure, compression set, elongation, tear and strength.

From this project, more investigation will be suggested in order to achieve the goals requested at the beginning of this TCS program.

KEYWORDS: SILICONE, SPONGES, FOAMS, BLOWING AGENT, EXTRUSION, MIXING, HAV

Acknowledgement

I would like to thank specially Dr. Allan Amass and Dr Wendy Amass for their help and supervision during the project.

I would like also to thanks Mr Andrew Zarebski and Mr James Harrison (company supervisor) for their assistance and understanding during the project.

I would like to express my gratitude to the directors, managers and colleagues from Primasil Silicone Ltd to let me carry out this research and for their help.

I would like to thank Mr David Britton for his help during the project.

And finally, I would like to thank particularly Mr James Crump from Primasil Silicones Ltd for his help along this project and also Richard Darwood, Maria Martinez-Velon and Dave Bray from Aston University for their help in using different equipments in Aston University.

Table of Contents

Chapter 3: Silicone Elastomers 34

List of figures

List of pictures

List of tables

Abbreviations

CBA- Chemical blowing agent
HAV- Hot Air Vulcan
HFC-
KTP-
LDPE-
PBA- Physical blowing agent
PDS-
PET- Polyethylene Tere
PP- Polypropylene

Chapter 1:

Introduction to silicon atom

1-1 Silicon (Si) in the periodic table

Silicon was discovered in 1824 by Berzelius and is represented by the symbol Si. Silicon is a non-metallic chemical element and is the second most abundant element in the earth's crust. For example, beach sand is largely silicon. Silicon makes up to 28% of the crust by weight where oxygen (most abundant element) makes up to 47%. The atomic number of silicon is 14 and its atomic weight is 28.0855. Si has a dark grey colour with a bluish tinge (c.f. picture 1) and is classified as semi-metallic.

Picture 1: Aspect of Silicon

Silicon is normally combined to other elements and can not be found pure. Si is content in many types of rocks and minerals such as sand, quartz, rock crystal, agte, mica. Si is used to make glass, concrete and semi-conductors.

Different covalent bonds can be formed with Si such as Si-H, Si-C, Si-O, Si-F, Si-Cl and Si-Si.

There is normally no need to make silicon in the laboratory as it is available commercially through the treatment of silica: SiO_2, which is treated with pure graphite (coke) in an electric furnace:

$$SiO_2 + 2\,C \longrightarrow Si + 2\,CO$$

Under these conditions, silicon carbide SiC can be formed. By keeping the amount of SiO_2 high, silicon carbide may be eliminated.

$$2\,SiC + SiO_2 \longrightarrow 3\,Si + 2\,CO$$

Another method can produce very pure silicon by the reaction of $SiCl_4$ with hydrogen:

$$SiCl_4 + 2\,H_2 \longrightarrow Si + 4\,HCl$$

1-2 Si and its components

Silicon reacts with different elements. The surface of lumps of silicon is protected by a very thin layer of silicon dioxide, SiO_2 formed by contact with the oxygen of the air. Silicon is more or less inert to further oxidation by air even up to about 900°C. At temperatures about 1400°C, silicon reacts with nitrogen, N_2, in the air as well as oxygen, O_2, to form the silicon nitrides SiN and Si_3N_4, and the silicon dioxide SiO_2. Reactions are shown below.

$Si(s) + O_2(g) \longrightarrow SiO_2(s)$

$2\ Si(s) + N_2(g) \longrightarrow 2\ SiN(s)$

$3\ Si(s) + 2\ N_2(g) \longrightarrow Si_3N_4(s)$

Silicon also forms compounds with metal and with non-metal elements such as carbon (silicon carbide), oxygen (silica) and oxygen plus a metal (silicates) which can be aluminium, magnesium, barium, calcium etc. Silicon also reacts vigorously with halogen, with sulphur (SiS_2) and with hydrogen (SiH_4). Halogens reacting with silicon are: fluorides, chlorides, bromides and iodides. The reaction occurs at 300 °C only for the fluorides. For the others, the reaction is done at room temperature. Reactions are shown below.

a- Fluorides:

$Si\ (s) + 2\ F_2\ (l) \rightarrow SiF_4\ (g)$

b- Chlorides:

$Si\ (s) + 2\ Cl_2\ (l) \rightarrow SiCl_4\ (g)$

c- Bromides:

$Si\ (s) + 2\ Br_2\ (l) \rightarrow SiBr_4\ (l)$

d- Iodides:

$Si\ (s) + 2\ I_2\ (l) \rightarrow SiI_4\ (s)$

1-3 Organo-silicon compounds [1, 2]

Compounds are called organosilicon compounds if they have at least one direct Si-C bond in the molecule. These compounds include monomeric and polymeric compounds containing Si-C bonds, Si-O-Si bonds and other types.

1-3-1 Monomeric organosilicon compounds

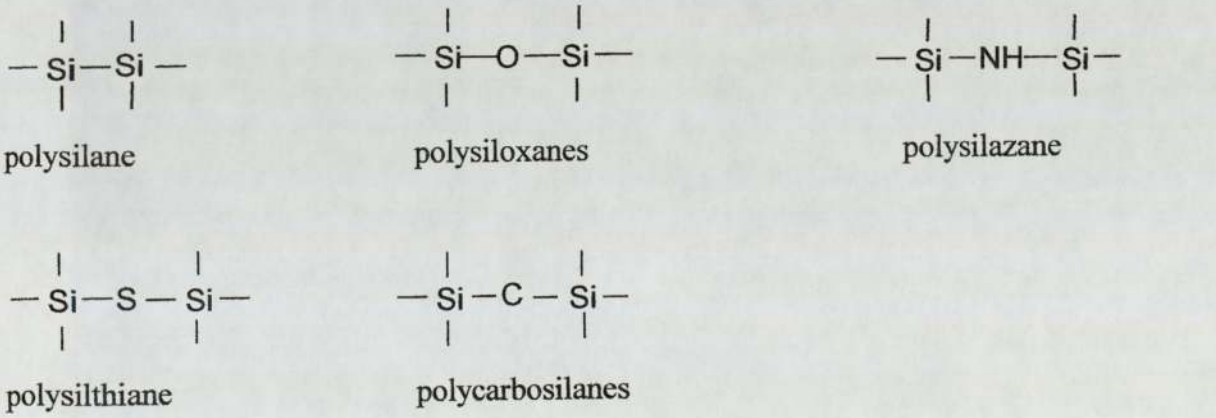
The compound is considered as a monomeric organosilicon compounds when one of the hydrogen atoms from SiH_4 has been replaced by an organic group (R) such as H_3SiR.

The other hydrogen atoms can stay as they are or be substituted by halogens, alkoxy, amino groups (X) such as H_2XSiR or HX'XSiR etc. Most common monomer has the formula R_nSiX_{4-n}. Tetraorganosilanes are not very useful in silicon chemistry. Tetramethyl- and tetraethylsilanes are the oldest. Organohalosilanes R_nSiX_{4-n} are the basic products of silicon chemistry and are used for preparation of siloxanes and for the synthesis of silanes with other silicon-functional groups. Other monomers can be organo(organooxy)Silanes $R_nSi(OR)_{4-n}$, organo-H-silanes R_nSiH_{4-n}, organosilanes with silicon-metal bonds etc.

1-3-2 Polymeric organosilicon compounds

The compound is polymeric when it has two units linked together. Monomeric compounds form the polymeric compounds by polymerisation.

If Si atoms are attached directly to another Si atom, the name of the class for the polymer is "polysilane". Other organosilicon compounds are shown below in figure 1. Polymeric organosiloxane compounds represent the actual silicone polymers. They are classified in four groups: linear polysiloxanes, branched-chain polysiloxanes, cyclic polysiloxanes and cross-linked polysiloxanes. Polysiloxanes are the polymers studied in this project.



$-\mathrm{Si}-\mathrm{Si}-$

polysilane

$-\mathrm{Si}-\mathrm{O}-\mathrm{Si}-$

polysiloxanes

$-\mathrm{Si}-\mathrm{NH}-\mathrm{Si}-$

polysilazane

$-\mathrm{Si}-\mathrm{S}-\mathrm{Si}-$

polysilthiane

$-\mathrm{Si}-\mathrm{C}-\mathrm{Si}-$

polycarbosilanes

Figure 1: Formula of polymeric organosilicon compounds

Chapter 2:

Introduction to silicones

Silicones are synthetic compounds containing silicon, oxygen and organic groups. Their chemical and physical properties depend on the silicon-oxygen-silicon skeleton. The most common is polydimethylsiloxane (figure 2).

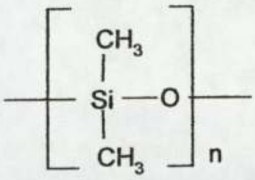


Figure 2: Chemical formula of Polydimethylsiloxane

2-1 Discovery of silicones [1-5]

The organosilicon chemistry's discovery started in 1840 by Dumas. Dumas predicted the possibility of existence of organosilicon compounds. Few scientists have been doing some research on Si compounds. The first aim of research on Si-C compounds was to find routes and methods for the preparation of the compound.

Buff and Wholer managed to form a low-boiling liquid (b.p. 28 °C) by passing an acid gas over a heated mixture of Si-C. The compound was containing Si, H and Cl but they didn't know the formula.

Later Friedel and Crafts found the formula which was $SiHCl_3$ (trichlorosilane). The first real tentative of producing Si-C compounds was also made by them. They prepared the first compound with organic group attached to Si atom by reacting diethyl zinc with silicon tetrachloride:

$$2\ ZnEt_2 + SiCl_4 \rightarrow 2\ ZnCl_2 + SiEt_4$$

Friedel carried on the research with Ladenburg but nothing exceptional was found.

In 1884, Pape managed to develop the reaction of trichlorosilane and silicon tetrachloride with dipropylzinc:

$$2\ SiHCl_3 + 4\ Zn(C_3H_7)_2 \rightarrow (C_3H_7)_3SiH + (C_3H_7)_4Si + 3\ ZnCl_2 + Zn + C_3H_8$$

In 1885, Polis synthesised aromatic derivatives of silicon:

$$SiCl_4 + 4\ RCl + 8\ Na \rightarrow R_4Si + 8\ NaCl$$

The major contribution on Si compound was done by Professor F.S. Kipping (1899-1944). Kipping published at least 54 papers on the subject. The major interest was in the chemistry of organosilicon compounds (isolation and characterisation of pure compounds). In 1904, he managed to prepare highly reactive chlorosilanes from silicon tetrachloride:

$$2\ C_2H_5MgCl + SiCl_4 \rightarrow (C_2H_5)_2SiCl_2 + 2\ MgCl_2$$

Kipping discovered the principle of intermolecular condensation of silanediols and silanetriols to polysiloxanes but he failed to recognize the importance of silicone polymerisation.

Polyorganosiloxanes are named "silicones". It came from Kipping. It is used to describe compounds with the formula R_2SiO by analogy to ketone.

From there, the development of silicon compounds has been carried on. More companies started to invest in research. At the end of the thirtieth, two groups from US: Corning Glass Work with J.F. Hyde and General Electric Co obtained a lot of interesting results. Rochow discovered a direct process to make silicones whereas Dow Corning used Grignard process for larger-scale development of silicones (both processes are explained later on).

The need of silicone in industry had increased, especially because silicones have an excellent heat resistance (better than organic rubber) and researchers tried to find other properties. A lot of new companies appeared after the World War II; silicones had been used in armaments (aircraft construction). After the war, companies opened in Europe too such as Wacker-Chimie and Bayer in Germany, Rhone-Poulenc in France, Midland Silicone in UK etc. The research on silicones was growing and is still very wide in the twenty-first century.

2-2 Preparation of chlorosilanes [1, 2 ,4]

Chlorosilanes are the intermediates from which siloxane polymers are prepared and are very active substances. Chlorosilanes can only be preserved in absence of moisture and are store under dry inert gases such as nitrogen. Chlorosilanes react by hydrolysis in the presence of water to give polysiloxanes. There are four preparations of chlorosilanes: direct process, Grignard method, olefin addition method and sodium condensation method.

2-2-1 Direct process

Rochow developed the "direct process". The simplest reaction can be described by:

$$2\,RX + Si \rightarrow R_2SiX_2$$

In reality more reactions occur in the system. The principle reactions are:

$$3\,RX + Si \rightarrow RSiX_3 + 2\,R\bullet$$

$$3\,RX + Si \rightarrow R_3SiX + X_2$$

$$2\,X_2 + Si \rightarrow SiX_4$$

Other compounds can be formed such as $RSiHX_2$ or R_2SiHX. To be more precise on the reaction, silicon is actually converted directly into chlorosilanes containing organic radical and chlorine. Methyl chloride is generally used and passes through a mixture of powdered Si and a copper catalyst heated to 250 – 280 C (Figure 3).

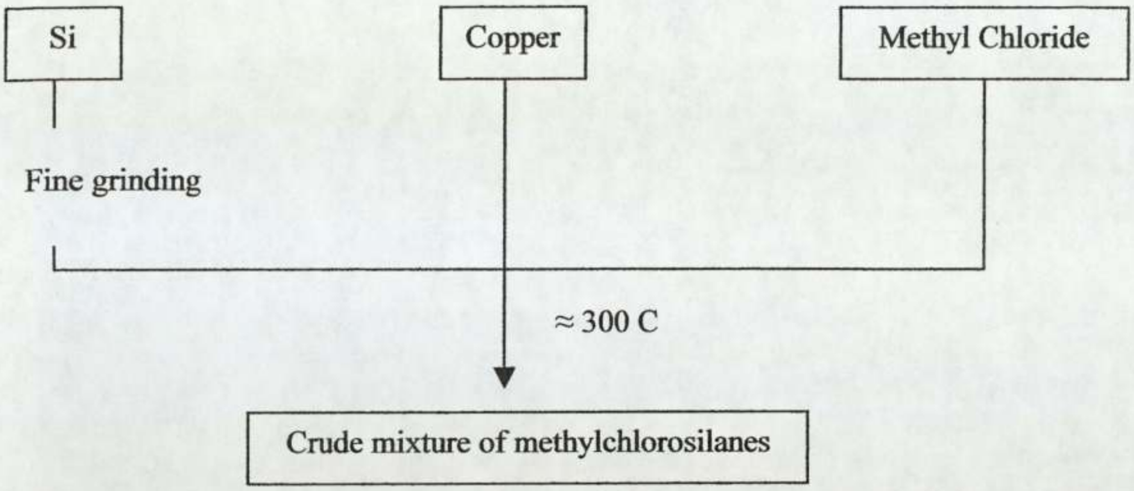


Figure 3: Illustration of direct process for preparation of chlorosilanes [1]

The control of the reaction is done by the choice of temperature, the rate of flow of methyl chloride, nature and quantity of catalyst. The function of copper is the formation of unstable copper methyl (CuMe) which gives methyl free radical. The free radical will reacts with silicon atom.

The main reaction is:

$$2\ MeCl + Si \rightarrow Me_2SiCl_2$$

2-2-2 Grignard method

The Grignard reaction was first applied by Kipping in 1904. Organomagnesium compounds help to transfer organic groups to silicon atoms:

$$RMgX + XSi\sim \rightarrow RSi\sim + MgX_2$$

The Grignard synthesis is in two-stage reaction. Alkyl or aryl halides and magnesium react to form the Grignard reagent:

$$MeCl + Mg \rightarrow MeMgCl$$

After the Grignard reagent will react with tetrachlorosilane and the reaction will give different compounds:

$$MeMgCl + SiCl_4 \rightarrow MeSiCl_3 + MgCl_2$$

$$MeMgCl + MeSiCl_3 \rightarrow Me_2SiCl_2 + MgCl_2$$

$$MeMgCl + Me_2SiCl_2 \rightarrow Me_3SiCl + MgCl_2$$

High yield of dimethyldichlorosilane is formed. Mixture of all products is filtred to remove solid $MgCl_2$ and distilled for the solvent. Figure 4 shows the complete reaction.

A wide range of organic groups can be attached to Si atom by this method. Normally, Si-H bonds don't react with the Grignard method. It depends on the solvent.

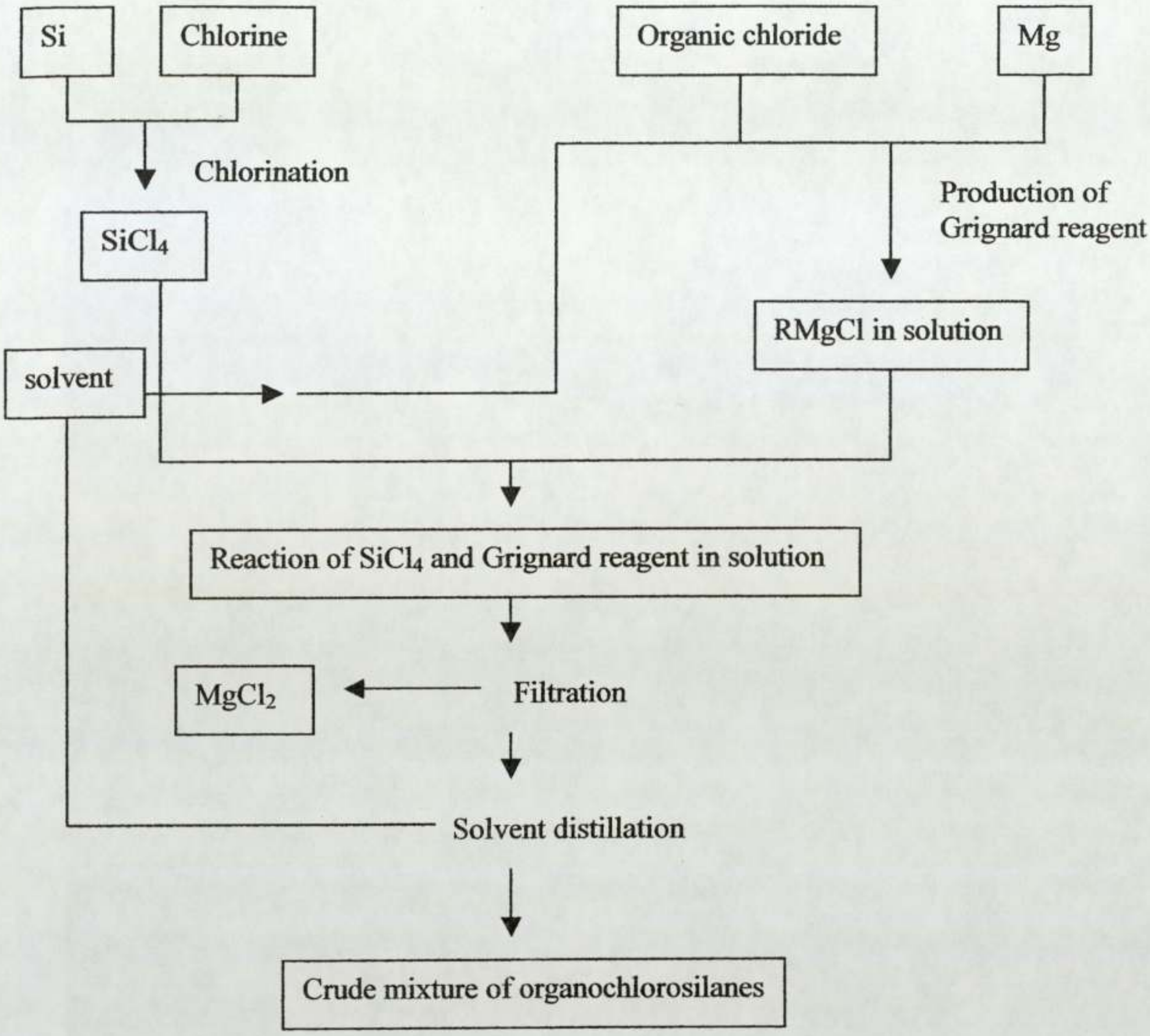


Figure 4: Illustration of Grignard method for preparation of chlorosilanes [1]

2-2-3 Olefin addition method

Compounds containing Si – H linkages such as $SiHCl_3$ and $MeSiHCl_2$ react under pressure with an unsatured organic compound. The reaction with olefins is catalysed by UV light and peroxides. Practically all olefins appear to be capable of adding Si-H bond.

Main reactions are:

$$A\bullet + SiHCl_3 \rightarrow AH + \bullet SiCl_3$$

$$RCHCH_2 + \bullet SiCl_3 \rightarrow RC\bullet HCH_2SiCl_3$$

$$RC\bullet HCH_2SiCl_3 + SiHCl_3 \rightarrow RCH_2CH_2SiCl_3 + \bullet SiCl_3$$

This method can not be used to prepare methylchlorosilanes.

2-2-4 Sodium condensation method

Silicon tetrachloride reacts with an organic chloride in the presence of sodium:

$$SiCl_4 + 4\,RCl + 8\,Na \rightarrow SiR_4 + 8\,NaCl$$

The reaction gives a low yield of SiR_4 and it is not valuable as the other methods.

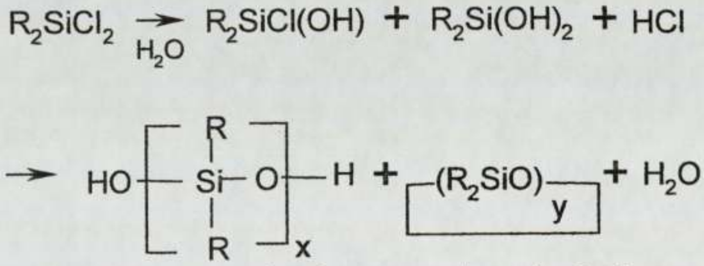
2-3 Preparation of polysiloxanes [1, 6]

There are four types of preparation for polysiloxanes: hydrolysis of chlorosilanes, equilibration of lower siloxanes, ring opening polymerisation reaction and special condensation polymerisation reaction.

2-3-1 Hydrolysis

This method is the most direct process of polysiloxanes. It consists of allowing organohalosilanes to run into an excess of water. The excess is adjusted to have no more than 20% of formation of aqueous hydrochloric acid. The by-products obtained are a mixture of linear and cyclic polymer. The composition depends on type and purity of chlorosilanes, on rate and order of addition of the components, on presence of basic or acid additives and on temperature of the reaction. The hydrolysis of chlorosilanes is usually a very fast reaction: exothermic which needs to be cooled down.

The hydrolysis has two steps. Monosilanols and disilanols are formed from dichlorosilanes. Secondly, a condensation reaction forms various siloxy products (figure 5).



$$R_2SiCl_2 \xrightarrow[H_2O]{} R_2SiCl(OH) + R_2Si(OH)_2 + HCl$$

$$\rightarrow HO\left[\begin{matrix} R \\ | \\ Si-O \\ | \\ R \end{matrix}\right]_x H + (R_2SiO)_y + H_2O$$

Figure 5: Hydrolysis reaction for preparation of polysiloxanes [1]

2-3-2 Equilibration

Equilibration is used for siloxanes redistribution process of linear and cyclic polymer. Si-O bonds can be attacked by ionic reagents and are possible to be broken. Other siloxanes linkages will be formed until thermodynamic equilibrium. The catalysts used can be bases or acids.

Examples for linear siloxanes:

$$\equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv + \mathrm{KOH} \qquad \equiv \mathrm{Si} - \mathrm{OH} + \mathrm{KO} - \mathrm{Si} \equiv$$

$$\equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv + \mathrm{KO} - \mathrm{Si} \equiv \quad \equiv \mathrm{Si} - \mathrm{OK} + \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv$$

2-3-3 Ring opening polymerisation reaction [7- 9]

High molecular weight polysiloxanes can be prepared by either acid or base initiated ring opening polymerisation reaction of cyclic siloxanes. The mechanism is anionic or cationic and gives linear polymers. The propagating active centre reacts with cyclic monomer molecules which lead to incorporate monomer unit into the growing polymer chain and to generate identical activity at the end of the new chain. The resulting polymers are various linear and cyclic chains with different distributions of molecular sizes. There are three different reactions: kinetic reaction, acid-catalyst reaction and the base-catalyst reaction.

First, the kinetics control the process. The ring opening polymerisation reaction occurs quicker than the equilibration reaction (figure 6): k1 > K2.

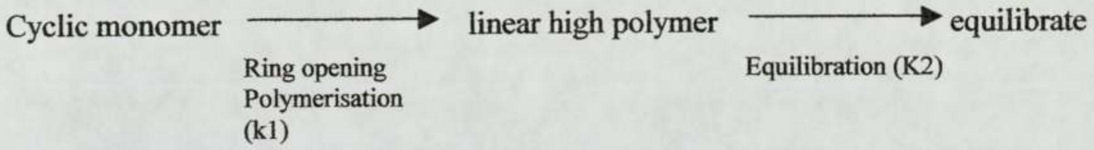


Figure 6: Kinetic and equilibration reactions for ring opening polymerisation

The second reaction is acid-catalyst polymer reaction of cyclic trimers. Two reactions are present and compete: the ring opening polymerisation and the cyclisation (figure 7).

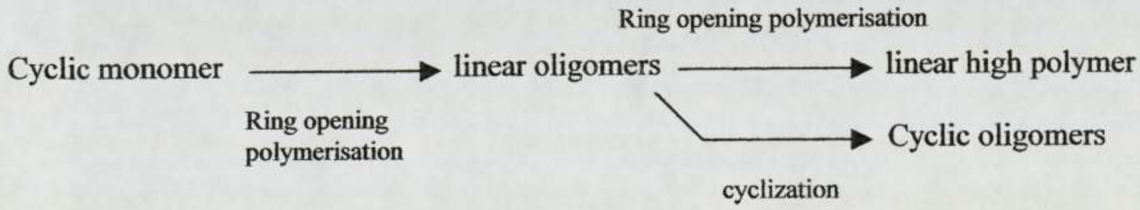


Figure 7: Acid-catalyst polymer reaction of cyclic trimer

The last reaction is base-catalyst reaction which proceeds similar as the anionic polymer but there are no formations of new cyclic products.

a- Anionic reaction

The anionic polymerisation is the principal method used for the preparation of high molecular weight and functional polysiloxanes. The initiator is normally hydroxyl or silanolate anions. The initiation is done by nucleophilic attack of the base on cyclic monomer which opens the polar siloxy bond. Propagation is the second step following by the termination of the polymers as shown on the figure 8.

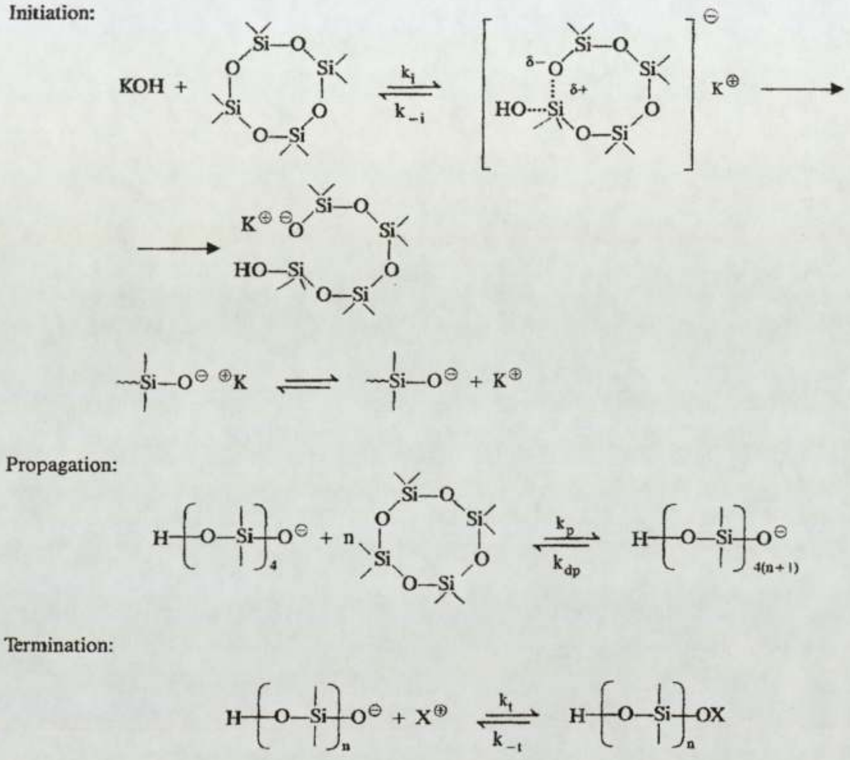


Figure 8: Anionic polymerisation for polysiloxanes [7]

b- Cationic polymerisation

This reaction is not very well understood. Scientists agreed on the following process. The cationic polymerisation has a reaction catalyst (CT) and a proton donating cocatalyst. It provides protons which are the initiator of the polymerisation. The catalyst can be protonic acid such as H_2SO_4 (most common) or HCl or Friedel-Crafts catalyst such as $AlCl_3$ or $FeCl_3$. Entire cyclic siloxanes monomer are added to active propagating centre as single unit in the ring opening polymerisation reaction (figure 9).

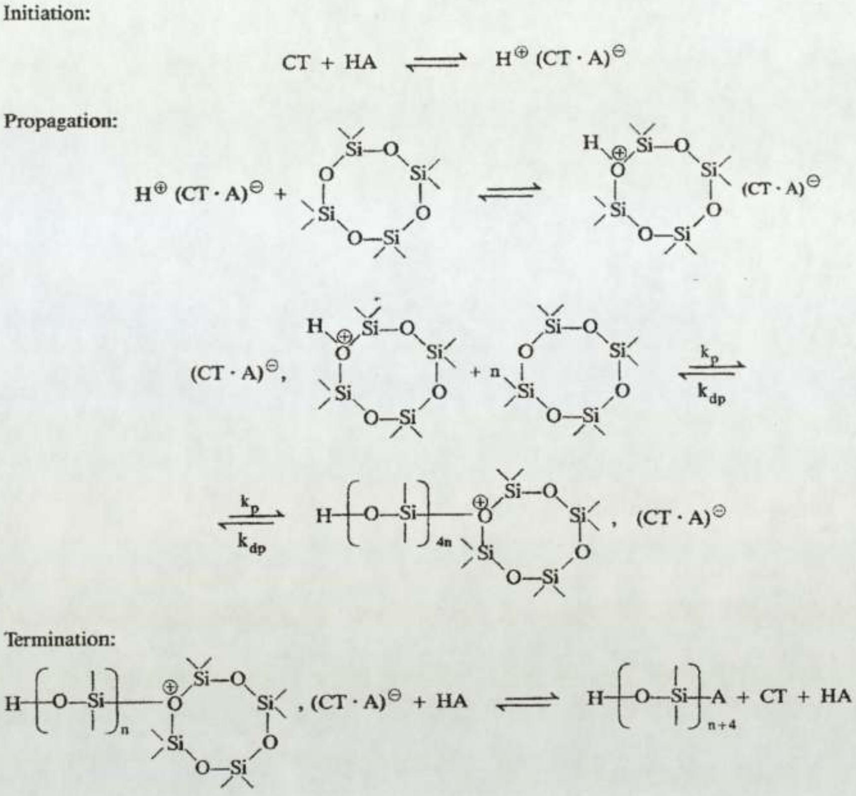


Figure 9: Cationic polymerisation for polysiloxanes [7]

2-3-4 Special condensation polymerisation reaction

Condensation reaction is used for the preparation of linear siloxanes polymers by application of various step-growths. Disilanols reacts with various difunctional monomers as shown in figure 10.

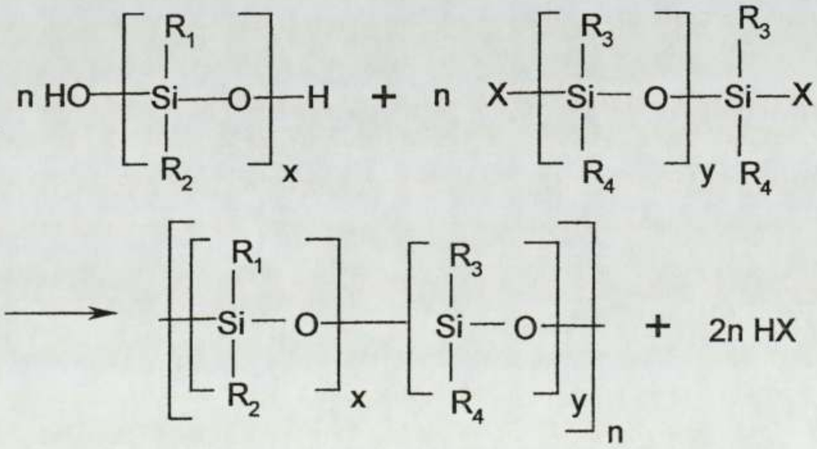


Figure 10: Condensation polymerisation for polysiloxanes

$R_{1,\,2,\,3\text{and }4}$ and y can vary widely whereas x is normally either OH, OR, Cl, NR_2 or O-CO-CH $_3$. [7]

This reaction is used for the preparation of block polymers where the size of x and y can vary. It is also used to modify siloxanes polymers by introducing new units into the polymer main chain.

2-4 Different forms of silicones

Three types of silicone form exist: silicone fluids, silicone resins and silicone elastomer.

2-4-1 Silicone fluids [1, 2, 4, 10]

Silicone fluid is a colourless liquid with very low viscosity. Its most important application is mould-release agent. Fluids can be divided in two categories: linear dimethyl silicone fluids and other silicone fluids. They are all straight chain polymers.

a- Preparation

Fluids are produced by blending distilled chlorosilanes which are hydrolysed (such as part 2-3-1). After decantation, the mixture contains long and short chains of siloxanes and cyclic siloxanes. The solution is equilibrated to get a balance of molecular distribution. The mixture is heated with a catalyst to get uniform molecular weight i.e. smaller chains become bigger and bigger chains become smaller. The solution is after decanted and neutralises for the pH. Finally, the fluid is heated to get volatile components of low molecular weight.

b- Properties

Fluids are colourless, odourless, practically non-volatile and non-toxic materials. They have high stability and are inflammable at high temperatures. Fluids are also inert to many chemical reagents.

c- Applications of fluids

Fluids are used to make mould-release agent, water repellent for textile and leather, anti-adhesive, water repellent for the treatment of paper, lubricant, grease and anti-foam. They are employed also in polish and paint additives.

2-4-2 Silicone resins [1, 2, 4]

The resins are characterised by three-dimensional branched chain structure.

a- Preparation

The chlorosilanes are hydrolysed as part 2-3-1. The raw material contains trifunctional monomers (differ from fluids and rubber). The ratio methyl and phenyl influences the properties of the resin. If the amount of methyl increases, the hardness of the final resin increases. If the amount of phenyl increases, the resistance to high temperature of the resin increases.

When the hydrolysis of chlorosilanes is completed, the mixture has two liquid layers: aqueous hydrochloric acid and organic solvent solution of low molecular weight silicones, which have to be separated. The mixture of silicones contains cyclic, linear and cross-linking polymers in silanol end-groups. To finish the preparation of the resin, the mixture is heated between 150 and 200°C. A condensation of silanol to form Si-O-Si linkage in three dimensions occurs by utilising a catalyst such as zinc, cobalt. The properties of the resin and the rate of cure will depend on the nature of the catalyst.

b- Properties

Resins are stable at high temperatures and have good resistance to most aqueous chemical reagents. They have poor properties for tensile strength, hardness, flexibility if they are compared to organic resins. They have also good electrical properties: insulation.

c- Applications

Resins are used for surface coatings, release agent, water repellents and electrical applications.

2-4-3 Silicone Elastomer [1, 2, 4]

Elastomers are based on linear polymers of very high weight analogous to silicone fluids.

Manufacture of silicone elastomer:

A pure difunctional monomer is obtained from the hydrolysis of chlorosilanes: high molecular weight free from cross-linking. In general, cyclic siloxanes are equilibrated in the presence of an alkaline catalyst at about 150 to 200 °C for several hours. The product is a colourless fluid which becomes very viscous on cooling at room temperature. The molecular weight of the elastomer can be changed depending on its uses. The original silicone elastomer is poly(dimethylpolysiloxane).

Copolymerisation is used in the preparation of silicone in order to improve the properties of the elastomer. Some dimethyl silicone can be added to the process to achieve low temperature flexibility as well as methyl vinyl silicone will give low compression set and fluorinated chains added to the polymer will improve the oil-resistance of the elastomer. From these silicone elastomers, silicone compounds can be produced. The manufacture of silicone rubber compound is discussed in the following part as its properties and its use.

Chapter 3:

Silicone Elastomers

All elastomers need to be cross-linked to achieve their mechanical properties which depend on the degree of cross-linking, on the chemical nature of cross-linking and on the condition of vulcanisation.

3-1 System of vulcanisation for elastomer [1, 7, 11, 12]

Cross-linking occurs at elevated temperatures and elastomers obtain their elastic properties after cure. The cross-link density influences the properties of the elastomer. The choice of cross-linking agent and the conditions of vulcanisation are both important.

3-1-1 Peroxides

The first way of vulcanisation is to add peroxides to the elastomer. Organic peroxides are normally utilised for silicone rubber. There are two classes of peroxides. Highly active peroxides are used for curing saturated polysiloxanes and other less active are employed if the rubber contains methyl or vinyl groups (table 1).

Highly active	**Critical temperature**	**Processing temperature**
Benzoyl peroxide	70 °C	125 °C
2,4 dichlorobenzoyl peroxide	60-70 °C	115 °C

Less active	**Critical temperature**	**Processing temperature**
Di-t-butyl peroxide	100 °C	160 °C
Dicumyl peroxide	100 °C	150 °C

Table 1: Examples of peroxides used to cure silicone compounds

Peroxides decompose with production of free radicals which promote the cure. The quantity used is normally 0.5 to 3 parts per hundred parts of rubber depending on the cross link density required, and hence the mechanical properties. Best results are obtained with 1 pph or less. The increase of curing agent concentration increases the hardness and the tensile strength of the rubber but decreases its elongation at break. $-Si-CH_2-CH_2-Si-$ and $-Si-CH_2-Si-$ linkages are formed during curing. The mechanism of peroxides cure is shown in the figure 11. Peroxides give free radicals which abstract hydrogen atoms from methyl groups. One cross-link is formed for each molecule of peroxide decomposed but by-product such as benzoic acid remains in the rubber. A post-cure is done for several hours at 200-250 °C to avoid it.

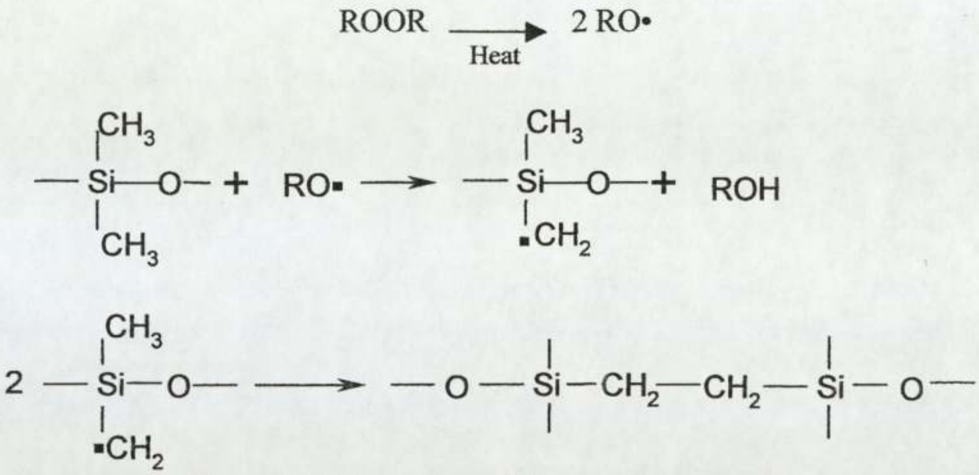
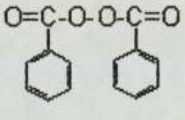
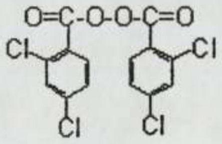
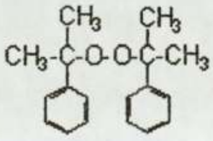


Figure 11: Mechanism of the peroxides cure [7]

Peroxides in a paste or liquid form are added to the uncured rubber on a two-roll mill. A list of peroxides is given below (table 2). Peroxides disperse homogenously in the silicone rubber at room temperature and the cross-linking takes place by applying heat. The amount of peroxides influences the processing conditions of the compound and its properties. The quantity and the use of peroxides limit the shelf-life of the compound.

Chemical name and formula	**Form**	**Comments**	**$t_{1/2}$ [8]**
DiBenzoyl peroxide 	• Powder, 80% active • Paste in phthalate plasticiser, 70% active • Paste in silicone oil, 50% active	Used for silicone rubbers; not suitable for olefin rubbers; dry powder explosive	At 100 C, 0.37 hr
Bis(2,4 – Dichlorobenzoyl) - peroxide 	• Powder, 50% active • Paste in phthalate plasticiser, 50% active • Paste in silicone oil, 50% active	Used for silicone rubbers; not suitable for olefin rubbers; dry powder explosive	At 80 C, 0.1 hr
Dicumyl peroxide 	• Powder, 95% active • Powder, 40% active • Solution in phthalate plasticiser, 50% active • Powder, 96% active	Used for natural and synthetic olefin rubbers, and silicone rubbers	At 100 C, 50 hr

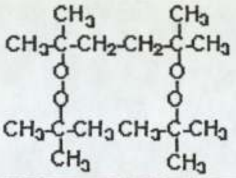
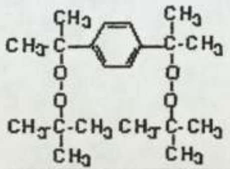
2,5 - Di - (t - butylperoxy) - 2,5 - dimethylhexane 	- Powder, 50% active - Powder, 45% active	Used for natural and synthetic olefin rubber, and silicone rubbers	At 100 C, 67 hr
Di - (t - butyl peroxy) - diisopropylbenzene 	- Powder, 85% active	Used for natural and synthetic olefin rubber, and silicone rubbers	At 100 C, 60 hr

Table 2: List of typical peroxides

3-1-2 Hydrosilylation

The second method of curing is carried out by hydrosilylation of unsaturated groups in polysiloxanes by polyfunctional silicone hydrides in the presence of metal catalyst such as a platinum compound. The reaction can take place at ambient temperature (RTV) or with heat (figure 12).

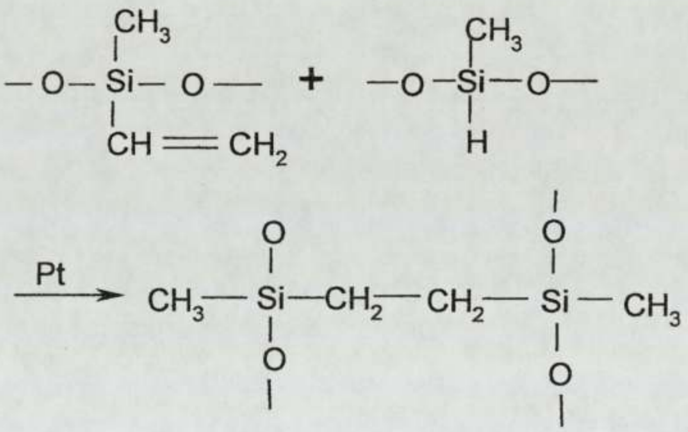


Figure 12: Cure of polysiloxanes by hydrosilylation [7]

3-1-3 Room temperature vulcanisation

The last possibility for vulcanisation is the room temperature vulcanisation (RTV). This process uses a condensation reaction of various silicon containing functional groups (silanol) which can react at room temperature, with or without a catalyst; to eliminate an alcohol. Catalysts are amines and carboxylic acid salts of metal (Pb, Fe, Zn, Ba…) and titanium is a good catalyst. The cure rate varies with OH content of siloxanols, the amount of cross-linking and catalyst whereas the mix can be affected by the temperature, moisture and pH. The cross linking reaction is shown below (figure 13). Y is normally $-OH$, $-OR$, $-NR_2$ or $-O-CO-CH_3$. X can be alkoxy, amino etc.

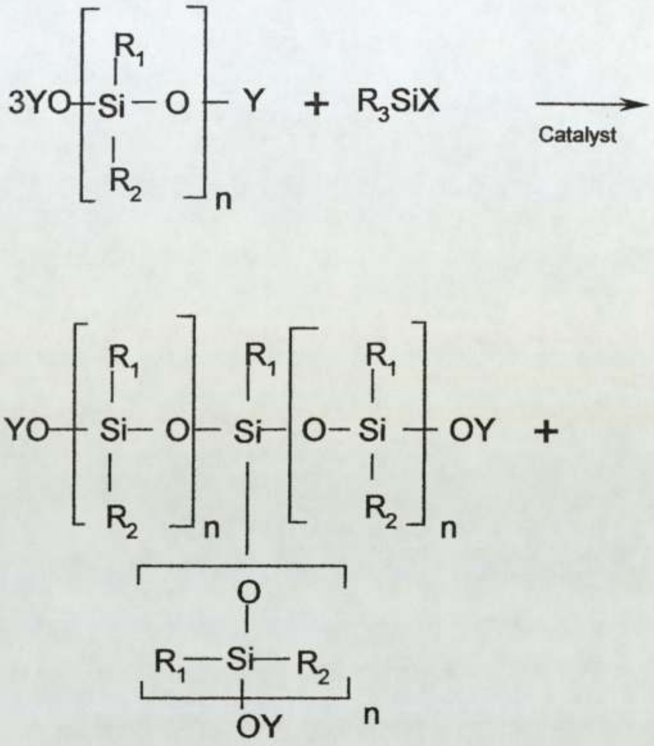


Figure 13: RTV cure for polysiloxanes [7]

3-2 Ingredients used for silicone rubber [12]

Silicone base is the principal component which is a mix of polysiloxanes. The rubber can have different properties: hardness, compression set, tensile strength… depending on the composition of polysiloxanes. The second ingredient added is a filler. Fillers are classified in three groups: reinforcing, semi-reinforcing and non-reinforcing fillers. Reinforcing fillers are used to increase hardness, modulus, tensile, tear and shear strengths. Semi and non-reinforcing fillers are utilised to reduce crack propagation and cost of the material. The reinforcing fillers for silicone rubber are treated silicas such as fumed silica. The semi and non-reinforcing fillers are natural silicates, quartz, clays and calcium carbonate. Carbon black is also a filler. Carbon black is only used when electrical conductivity properties are required because carbon black is difficult to mix and reacts with some peroxides. Processing aids are other ingredients and are used in the rubber industry to facilitate the processing of polymers (oil, resins). Curing agents are very important ingredients, used to cure the rubber (see above part 3-1). Accelerators and retarders can be used to increase or to reduce the rate of cross-linking reaction. Antioxidants are also sometimes used to prevent the oxidation reaction of the compound in the presence of oxygen or ozone. Pigments are utilised to give a colour to the compound, often used in master batches to obtain a good dispersion. Additives (red iron oxide, zinc oxide etc) can improve different properties of the elastomer. Red iron oxide improves the heat resistance of the compound. Zinc oxide gives good heat conductivity. Aluminium hydrate provides electrical resistance to the rubber. The last ingredient which can be added is blowing agent when foam products are manufactured (see part 4).

3-3 Mixing and processing of silicone rubber [12, 14]

Silicone rubber compounds are processed on the conventional machines of the rubber industry. The equipment needs to be clean in order not to change the properties of the final product.

3-3-1 Mixing of silicon rubber

Two-roll mill will be used to mix and to preform the uncured compound. Two-roll mill has got two heavy rotating rollers made of cast iron, with surfaces of hardened stainless steel. One roller is rotated faster than the other: ratio 1.2/1 to 1.4/1 and the space between the two rollers can be varied. The rollers are cooled by water to keep the temperature under 40 °C in order to prevent scorching, loss of peroxides or early cure of the compound. Figure 1 of a mill shows a typical two-roll mill (Also appendix). The direction of rotation of the rollers is opposite (see figure 14).

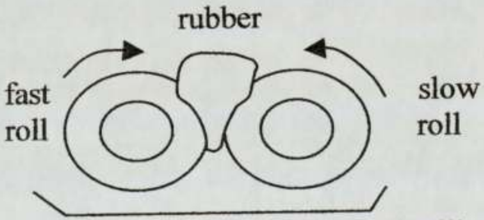


Figure 14: Illustration of a two-roll mill

The rubber is added first on to the mill, followed by the fillers and additives which can be added to the silicone compound. The master batches are next and finally the curing agent is introduced into the mix. When the compound is mixed homogeneously, it is taken out as sheet or dolly form and wrapped in a polyethylene sheet. Compound with highly reinforcing fillers should be re-freshing before use.

3-3-2 Processing of silicone rubber

a- Moulding:

- Compression moulding:

Compression moulding (figure 15) may be used for moulding silicone parts. In general, a preform is placed on the half of a bottom heated of the mould. The mould is closed under pressure causing the rubber to flow to all parts of the cavity. The application of heat and pressure accelerates the cross-linking reaction. The part is then ejected from the mould when it is still hot. A release agent can be applied on the mould before any moulding which helps to take the part out of the mould.

The temperatures are different between the press platen and the mould. The temperatures in the platen press are normally 130 to 150 °C to achieve 115 to 120 °C in the mould. The press platens are controllable at ± 3 °C. The temperature in the mould depends also on the size of the mould and the residence time of the mould in the press. There are three variables in moulding: pressure to close the mould, the speed of closing and the time of cure. Benzoyl peroxide and 2,4-dichlorobenzoyl peroxides are used because of their low rate of reaction so the time of cycle is short. Mould time depends on the curing agents and the thickness of the part. Moulding pressure needs to be enough to flow the material rapidly into the mould. The moulds are closed by hand or automatically and are made with stainless steel because it gives good finish to the parts. Compression moulding is used to make gaskets, seals, O-rings, flat sheets, others.

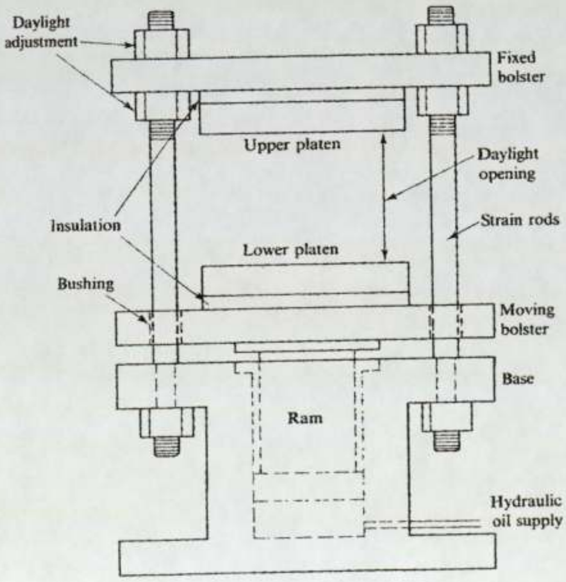


Figure 15: Compression moulding press [14]

- Transfer moulding:

Transfer moulding (figure 16) is a widely used technique which has faster cycles than compression moulding. A single preform is utilised per shot in transfer moulding whereas in compression moulding, more than one preform can be used. Transfer moulding can be operated with complex moulds. There are two types of mould; a pot and piston mould and a plunger mould. A pot and piston mould has a single ram compression press where a plunger mould has a double ram press, one to clamp the mould and the other one to transfer the unvulcanised rubber. Transfer moulding press can be operated by hand, semi-automatic or automatic.

Uncured rubber is positioned in a chamber at the top of the mould and pressure is applied. The mould closes and forces the rubber to flow in the heated mould. Time and temperature of moulding are similar to the ones used in compression moulding. Transfer moulding is applied to make gaskets, closures, "O" rings, diaphragms, seals, oxygen masks, electrical connector insulators etc.

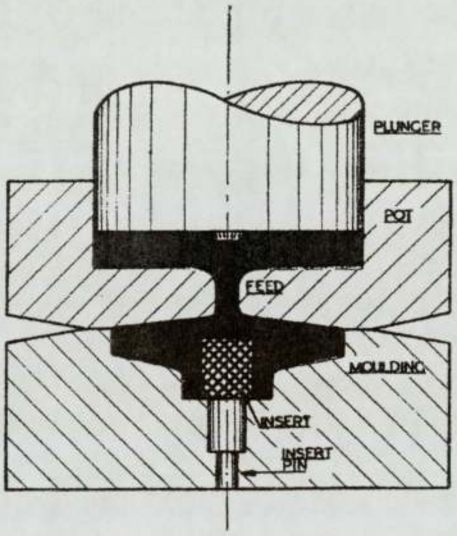


Figure 16: Transfer moulding press [14]

- Injection moulding

Rubber is automatically fed in strip to the screw of the injection moulding machine. The material is heated and plasticised by the warm screw in the barrel. The screw rotation creates further heat and softening as the rubber is sheared between the screw and the cylinder. When the volume of rubber accumulated at the front of the screw is equivalent to the volume of the mould cavity, the rubber is transferred to the mould. The screw, not rotating, now acts as a ram and forces forward the rubber by action of hydraulic pressure. When the rubber has filled the mould, a low pressure is held to prevent flashing. The vulcanisation takes place. During vulcanisation, the screw is automatically set to rotate again and charges fresh rubber ready for the next injection. When the vulcanisation is finished, the mould opens and the rubber part is automatically ejected. The mould closes again, ready for the next injection, during a short moulding cycle. Higher temperature peroxides are preferred because others tend to scorch. Injection pressure is between 500 and 2000 psi; depending on viscosity, size of injection nozzle, mould and injection time. Injection time depends on mould cavity size, injection pressure. Injection needs to be short in order to minimise scorch and moulding time. The cycle includes mould closure, injection advance, injection, cure, injection retract, mould opening, ejection of the part. The times of opening and closing the mould are set up at the beginning of the process. Screw speed, back pressure, injection pressure and rate of injection are controlled by hydraulic pressure. The barrel temperature is thermostatically controlled by water. The function of the screw is to plasticise the rubber and to transfer it. The injection pressure controls the mould filling operation. Horizontal and vertical moulds are possible to be used (scheme 17-18).

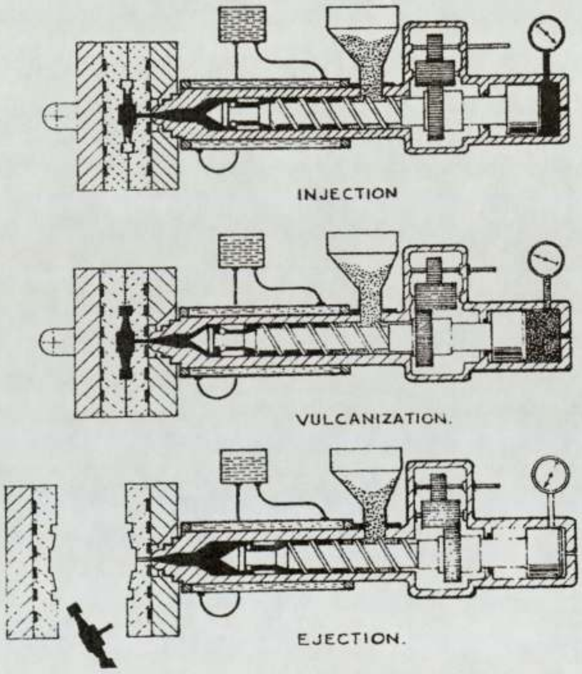


Figure 17: Injection moulding with vertical mould [14]

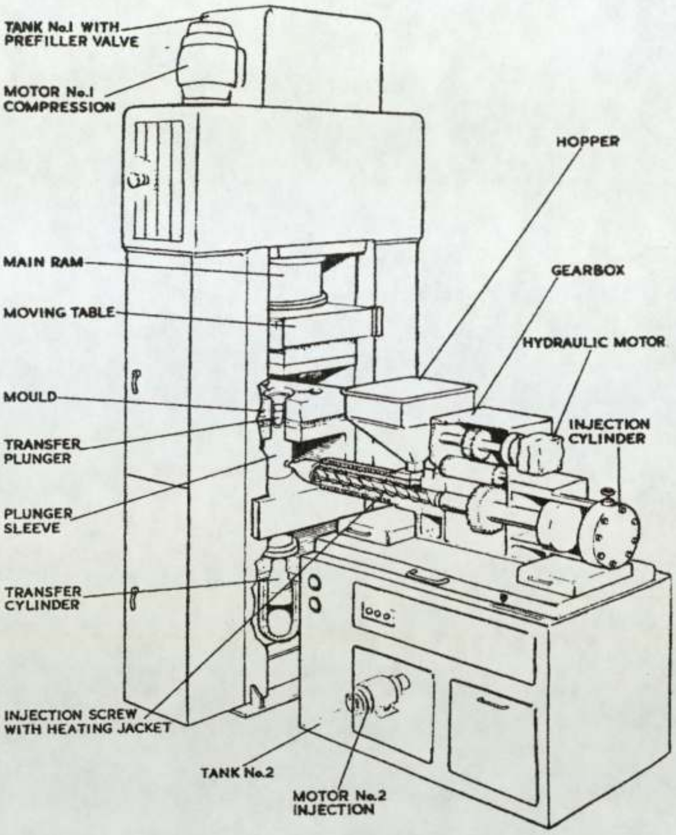


Figure 18: Injection moulding with horizontal mould [14]

b- Extrusion

Extrusion (appendix 2) is used to make tubing, rods, gaskets, seals, wire insulation and preforms used in compression moulding.

The extruder is composed of the barrel, the screw, the break plate and the die. The speed of the screw is variable. The most popular extruder has the following dimensions. The diameter of single flight screw is 83 mm with a length to diameter ratio of 10 or 12 to 1. The compression ratio in the extruder is 1:1.15 to 1:2. The flights are 13 mm deep. Double flight are utilised at the end of the screw to avoid too much back flow from the compound. The clearance between the barrel and the screw is 0.08 mm. The size of the barrel depends on the size of the screw. The barrel and the screw must be water cooled in order to avoid loss of curing agents or scorching. A gear extruder which is two feeding rolls is placed at the entrance and rotates the screw at the desired speed. Roller feed can be used in order to ensure a more uniform extrusion than hand feeding. There is a breaker plate placed at the end of the extruder which is a metal disc perforated with holes and recessed to hold various stainless steel screens. The screens filter out dirt, large particles and undispersed filler aggregates and create back pressure which reduces porosity. The last parts of the extruder are the dies, pins and die holder, which are in stainless steel. Stainless steel is economic and gives good finish.

Dies are design to produce good flow with no dead spaces. When tubes are extruded, air passes in the middle of the pin to prevent the tube from collapsing. Dies have to be smaller than the extruded part wanted because the material swells (3%) after extrusion. The dimension of the extruded part can be modified by changing the die, the characteristics of the material, the pressure in the extruder and by slowing or increasing the speed of the extruder. For extruding shape, the orifice of the die is different from the cross section of the extruded part.

The extruded part is immediately cured after extrusion for silicone rubber. A Hot Air Vulcanisation (HAV) system is placed after the extruder. The extrudate goes in a heated tunnel on a conveyor belt which is made of stainless steel mesh. The length of the HAV is normally a tunnel 7 to 9 meters long and heated by convection. The tunnel can have two to more heating zones. The temperatures of HAV go from 200 to 500 °C. Fresh air is also introduced in the tunnel. Turbulence gives faster heat transfer, a faster cure time and moves out the volatile gases. Vertical vulcanisation can be employed if the horizontal vulcanisation leaves impression from the conveyor belt on the extruded part. The maximum length of the vertical tunnel is 3 meters. HAV requires the use of 2,4dichlorobenzoyl peroxides, because other curing agents are too volatile. The influence of rate for the production of extruded parts depends on size and power of the extruder, on the design of the screw, on the clearance between the barrel and the screw, on the use of filler in the compound, on the type and length of HAV and on the shape of extruded part.

c- Calender:

Calender is used to produce sheets of unsupported silicone rubber and to apply silicone rubber to one or both sides of reinforcing fabrics. The most used calendar is three-rolls (figure 19).

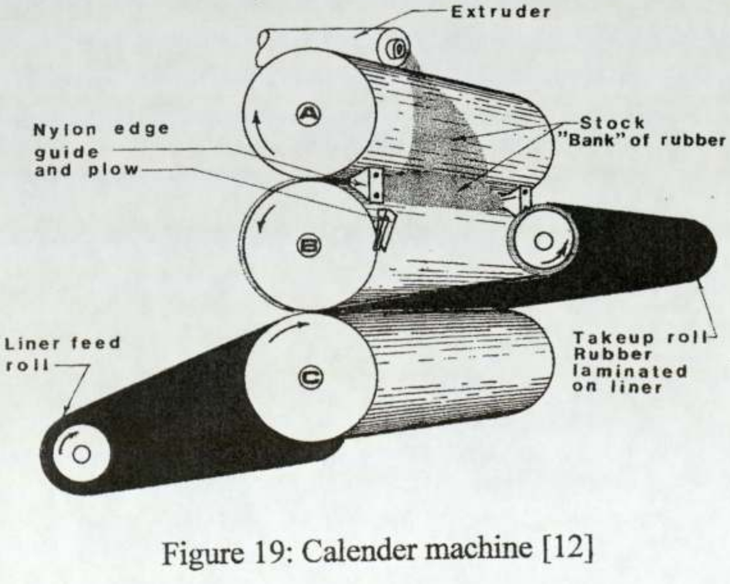


Figure 19: Calender machine [12]

Only A and C rollers can be moved. B roller turns faster than A roller by ratio 1.1:1 to 1.4:1; C roller has the same speed as B roller. Different speeds can be set for different formulations. There is a constant bank of rubber placed between A and B rollers. The temperatures of the rollers are controlled, with top roller is at to 50 °C; the middle roller is at room temperature and the bottom roll is water-cooled. The speeds and the temperatures are adjustable. Polyester film is run between the two lower rolls. If the calender process is used for the coating of fabric, the fabric is put between B and C roll in place of the polyester film. A four-rollers calender is used to coat both sides of fabric. The calendering production speeds range varies from 1.5 to 3 m/min. The vulcanisation of the compound can be carried out in an oven at a fixed temperature and for a fixed time, depends on the formulation and use of the product.

The silicone rubber sheets are used for manufacture of stamped-out diaphragms gaskets, flexible electric heating pads, pads for heat sealing equipments etc. Unvulcanised reinforced sheet are used to build hoses and reinforced seals or to mould diaphragms.

3-4 Properties of silicone elastomer [1, 2, 12]

Silicone rubber has a very low glass transition temperature (Tg), example: polydimethylsiloxane, -123 °C. The useful temperature range of silicone rubber varies from -100 °C to 300 °C depending on grade.

3-4-1 Mechanical properties

The tensile strength of silicone rubber goes up to 105 kg/cm^2 and measures the material's stiffness. The tensile strength is inferior to other type of rubber at room temperature but is higher then the other rubber at higher or lower temperature than the room temperature. The elongation of silicone rubber varies between 250 and 800 % and depends on the process and the cure of the rubber. The tear strength is generally around 10 to 20 kg.

The compression set, which is expressed as a percent, measures the failure of standard buttons (see testing part 7-6) to return to their original thickness after being subjected to a compressive stress force for a given period of time. The resistance of silicone rubber to compression set is around 7 to 10 %.

The hardness range of silicone is 25 to 75 shores A but softer and harder base are possible. The specific gravity of silicone varies between 1.1 and 1.6.

3-4-2 Electrical properties

Silicone has good insulation properties at room temperature when additives are added to silicone compound but has better results at elevated or lower temperature than the room temperature. Dielectric strength depends on the temperature range and on the thickness of sample. If the thickness increases, the dielectric strength decreases. Ground mica and glass can be added to silicone in order to help reducing the flammability of silicone. Silicone rubber burns to give silica and forms a non-conducting ash i.e. an insulating silica skeleton whereas organic rubber gives conducting carbon.

3-4-3 Thermal properties

The thermal conductivity (K) is an important property of silicone rubber and is two to three times higher than organic rubber and contributes to faster cure. The thermal conductivity range varies between 0.07 and 0.2 cal/sec/cm^2/cm/°C. The thermal conductivity increases with adding a filler such as "Minusil" (silica type filler). For higher values of K, zinc oxide or silver can be added. Silicone is an excellent insulator.

3-4-4 Heat resistance

The elongation and tensile strength of silicone do not vary after exposure for several hours at 180 °C or after a short time at 300 °C. Two processes can occur between 150 and 180 °C. First, organic groups split under influence of oxygen which increases the degree of cross-linking and the hardness of the rubber. The second process is the depolymerisation of high molecular weight linear polysiloxanes. For temperatures above 200 °C, the first process happens.

3-4-5 Chemical behaviour

Silicone rubber is very resistant to water from 0 to 100 °C. Mineral oil can cause swelling at elevated temperature. Silicone also swells in many organic solvent (aliphatic, aromatic).

3-4-6 Permeability to gases and to liquids

Silicone rubber's permeability is 10 to 100 times greater than the permeability (table 3) of other organic elastomers. Silicone rubber is permeable both to gases and to liquids.

	Air	N_2	CO_2
Natural rubber	400	360	2100
Silicone rubber	4100	3600	15000

Table 3: permeability for gases in $10^{-9} cm^2 sec^{-1} atm^{-1}$ at 50 °C [1]

3-4-7 Resistance to ozone and weather

Silicone is practically completely resistant to the action of oxygen, ozone and weather. The tensile strength loses 50 % and the elongation break within 5 years. Ultraviolet irradiation does not have effects on silicone rubber.

3-4-8 Inertness

Silicone rubber is odourless and tasteless and does not cause deterioration of other materials with which it comes into contact.

3-4-9 Surface properties

By using bonding compounds, silicone can be adhesively bonded to metals, glass, ceramics, fabrics etc. during vulcanisation. Siloxanes with alkoxy groups or Si-H bonds are particularly suitable.

3-5 Uses of silicone elastomer

Silicone rubber is used for its constant properties for a wide range of temperature: -80 °C to 250 °C, for its good electrical properties and its inertness. Silicone rubber is used for different applications such as aircraft industry, automotive, appliance, electrical and medical.

3-5-1 Aircraft

The aircraft is the biggest consumer of silicone rubber. Silicone is used because of its resistance to extreme temperature. Typical applications of silicone in aerospace are airframe opening seals, electrical connectors, cable insulation, gaskets and sealing rings for jet engines, oxygen masks and sealing strip for doors and windows.

3-5-2 Automotive

Silicone rubber is used for transmission shaft seal because it is resistant to hot transmission and to fluid and frictional heat of the shaft on the seal lip. The neutral nature of silicone prevents corrosion on the shaft. Silicone is also used for wire insulation and spark plug boots.

3-5-3 Appliance

Silicone is used for its excellent electrical properties and the retention of seal at high temperatures. Silicone gaskets, electrical insulator and seals are used in coffee pots, electrical frying pans and steam irons.

3-5-4 Electrical

Silicone is used for insulation of electrical conductors because of its good dielectric properties. The applications are wire and cable, high voltage application, embedding heating elements etc. The cables can be reinforced by fabrics.

3-5-5 Medical

Silicone is used because of its inertness and resistance to aging under environmental conditions. The market is growing for silicone rubbers in medical and pharmaceutical applications based on their heat resistance, lack of toxicity and physiological inertness. The applications are blood transfusion tubing, drainage tubes, babies' feeding bottle teats and human implants.

Chapter 4:

Blowing agents and sponge

4-1 Blowing agents [15, 16]

Blowing agents are used in the production of extruded foamed products and for cost savings, light weight and good thermal insulation effect. The products made with blowing agents are utilised in appliance, construction, food processing and packaging. Blowing agents are used in injection moulding and extrusion processes.

Blowing agents can be either physical blowing agent (PBA) or chemical blowing agent (CBA). PBA are injected into the process as liquid or gases whereas CBA decompose to generate gases during processing. PBA can be low boiling point liquids such as pentane or isopropyl alcohol and remain liquid in the melt compound when the melt is under pressure. When the pressure reduces, PBA changes from liquid to vapour and the compound then expands. Other PBA are inert gases such as carbon dioxide or nitrogen. The gases dissolve as vapours in the melt material and expand the compound. CBA utilises a decomposable material which produces a gas or gases by decomposition under processing conditions.

4-2 PBA

In the early development, PBA were used to produce polystyrene foams. First, low boiling point liquids were used such as methyl chloride or butylenes. Later on, direct gases processes were developed. LDPE, PP, PET and other plastics are used with PBA to produce foam products. Physical blowing agents can be low boiling liquids or pressurised gases. Hydrofluorocarbons (HFCs) and hydrocarbons are often used. Hydrocarbons are expensive and flammable products whereas hydrofluorocarbons are not. The disadvantage of hydrofluorocarbons is that they attack the Earth ozone layer due to the presence of fluoro atoms. PBA dissolve in the polymer when temperatures and pressure are employed and give a closed-cell foam structure. Few steps are important in this process. The system must be capable of melting, mixing the polymer and additives, dissolving and dispersing the PBA, cooling the melt containing the PBA and maintaining sufficient pressure until extrusion of the compound.

Several properties for PBA are also important such as to be inertness, safe, economical and to have a boiling point of –10 °C to +65 °C, adequate solubility in molten resin, low permeability through resin and low solubility in solid resin. The boiling point of PBA is essential and needs to be below the processing temperature in order to expand the polymer. Once the foam is formed and cooled to room temperature, the PBA should have sufficient high boiling point to maintain sufficient pressure inside the foam cells to keep the foam from collapsing. A list (table 4) of PBA is given below. The lower density of foam achieved with PBA is 0.15 g/cm^3. None of physical blowing agents are environmental friendly.

Name	Formula	Cas#	MW	Boiling Point, C	Vapor Pressure, psi @ T C	Liquid Density, g/cc	Thermal Conductivity, W/mK	Flamable
Propane	C_3H_8	74-98-6	44.1	-42.1	137.89	0.49	0.0179	Yes
n-Butane	C_4H_{10}	106-97-8	58.1	-0.5	35.26	0.55	0.0159	Yes
i-Butane	$CH_3(CH_3)CHCH_3$	75-28-5	58.1	-11.7	50.53	0.55	0.0161	Yes
n-Pentane	C_5H_{12}	109-66-0	72.2	36.1	9.9	0.621	0.0141	Yes
i-Pentane	$CH_3(CH_3)CHCH_2CH_3$	78-78-4	72.2	27.0	14.3	0.615	-	Yes
HCFC 22	CHF_2Cl	75-45-6	86.5	-40.8	151.4	1.194	0.0106	No
HCFC 142b	CF_2ClCH_3	75-68-3	100.5	-9.2	49.16	1.11	0.0108	Yes
HFC 152a	CHF_2CH_3	75-37-6	66.0	-24.7	86.81	0.899	0.0136	Yes
HCFC 123	$CHCl_2CF_3$	306-83-2	153.0	27.1	13.27	1.46	0.0095	No
HCFC 123a	$CHFClCF_2Cl$	354-23-4	153.0	28.2	12.61	1.467	0.0111	No
HCFC 124	$CHFClCF_3$	2837-89-0	136.5	-12.0	55.85	1.356	0.0106	No
HFC 134a	CH_2FCF_3	811-97-2	102	-26.5	96.52	1.207	0.0127	No
HFC 143a	CH_3CF_3	420-46-2	84	-46.7	182.5	1.089	0.0137	Yes
CFC 11	$CFCl_3$	75-69-4	137.4	23.8	15.32	1.476	0.0082	No
CFC 12	CF_2Cl_2	75-71-8	120.9	-29.8	94.51	1.311	0.0100	No
CFC 113	$CFCl_2CF_2Cl$	76-13-1	187.4	47.6	6.46	1.565	0.0097	No
CFC 114	CF_2ClCF_2Cl	76-14-2	170.9	3.6	30.96	1.456	0.0112	No
MeCl	CH_3Cl	74-87-3	50.5	-24.2	82.16	1.098	0.0106	Yes
MeCl2	CH_2Cl_2	75-09-2	84.9	40.1	8.22	1.322	0.0084	No
Carbon Dioxide	CO_2	124-38-9	44.0	-78.5	N/A	N/A	0.0165	No

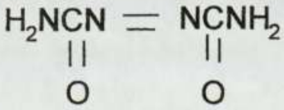
Nitrogen	N_2	7727-37-9	28.0	-195.8	N/A	N/A	0.0258	No
Oxygen	O_2	7782-44-7	32.0	-183	N/A	N/A	0.0266	No

Table 4: list of PBA, no flammable peroxides are written in blue and flammable peroxides in red

4-3 CBA

Their history is based in explosive and bakery products. Chemical blowing agents are organic or inorganic compounds and are solid or liquid material. They decompose at elevated temperatures producing gas in melted polymer and their range temperature needs to be the same as the temperature to melt the resin to avoid premature or incomplete decomposition of the CBA. The choice of chemical blowing agents depends on foaming gas and decomposition temperature. CBA are homogenously mixed with the melt polymer before decomposition temperature is achieved. The temperature control is critical to obtain good foam production. CBA generates carbon dioxide or nitrogen gases. Carbon dioxide produces finer cells, lower density and better surface than CBA producing nitrogen. Nitrogen is mostly used for injection moulding. Chemical blowing agents can be endothermic or exothermic. Exothermic CBA generate thermal energy (heat) during their decomposition and it is difficult to stop them when they start to decompose. Exothermic CBA have a fast decomposition in a narrow range of temperature and produce nitrogen gases. Endothermic CBA consume thermal energy during their decomposition and require additional heat to support their decomposition. They generate carbon dioxide gases and have a broader decomposition time and temperature range than exothermic CBA. Two examples of CBA are described below. Other CBA are listed in the table 5. The lowest density achieved with CBA is 0.50 g/cm^3.

The first CBA is azodicarbonamide which decomposes around 205 to 215 °C. Activators such as zinc oxide or zinc stearate may be used to lower its decomposition temperature by 40 °C. The reaction of azodicarbonamide can leave residual materials on die and mould tooling.
Its chemical formula is:



$$H_2N\underset{\underset{\displaystyle O}{\|}}{C}N = N\underset{\underset{\displaystyle O}{\|}}{C}NH_2$$

Azodicarbonamide decomposes to give gases: 65 % of nitrogen, 24 % of carbon oxide, 5 % of carbon dioxide, 5 % of ammonia and solid decomposition materials which include cyanuric acid, urazol etc. The gas yield is 220 cc/gm. This CBA is FDA approved with a maximum level of 5 %.

The second and most used CBA is a blend of citric acid and sodium bicarbonate. It is generally blended in stochiometric proportion and exposure to moisture needs to be prevented. The equation of decomposition is:

$$C_6H_8O_7 + 3\,NaHCO_3 \longrightarrow (C_6H_5Na_3O_7).2\,(H_2O) + 3\,(CO_2) + H_2O$$

The reaction takes place in two temperature range: 160 and 210 °C. The gas yield is 120 cc/gm. This blowing agent is FDA status.

Name	Chemical name	Endo or Exo	Decomposition temperature C	Gas evolution cc/gm	Gas
Citric acid / sodium bicarbonate		Endo	160-210	120	CO_2
ADCA	Azodicarbonate	Exo	205-212	220	N_2
OBSH	p-p'-Oxybis (benzene)sulfonyl hydrazide	Exo	158-160	125	N_2
TSH	p-toluene sulfonyl hydrazide	Exo	110-120	115	N_2
TSS	p-toluene sulfonyl semicarbazide	Exo	228-235	140	N_2
DNPT	Dinitrosopenta-methylenetetramine	Exo	190	190	N_2
5PT	5-phenyltetrazole	Exo	240-250	220	N_2
SBH	Sodium borohydre	endo		2000	H_2

Table 5: List of CBA used to make foams

4-4 Future of blowing agents

A constant search for environmental friendly PBA is in progress. CBA are also constantly being modified by reformulation or blending. The use of master batches improves the accuracy of dosing the CBA. Interactions between blowing agent and the rest of the process can be complex. Good foams can be produced when the choice of blowing agent, polymer, equipment and processing parameters have been chosen carefully.

4-5 Sponges [12, 15]

A sponge is the result of adding a blowing agent which decomposes during the cure to give cell structure to a compound. Two forms of foam are possible: thermoplastic foams and thermoset foams (table 6). The applications of foam include: thermal and acoustic insulation, core materials for sandwich panels, flotation materials, food containers, labels, protective packaging, cushioning, wire and cable jacketing and casketing. The production of thermoplastic foam (polystyrene) and thermoset foam (urethane) are shown in this part before the production of silicone foam. The aim of this is to present different processes of foams. The structure of the foam can be open-cells, closed-cells or a mix of both.

Thermoplastic foam	**Thermoset foam**
Polystyrene	Polyurethane
PVC	Phenol-formaldehyde
Polyolefins	Epoxy
ABS	Silicone

Table 6: Examples of thermoplastic and thermoset foams

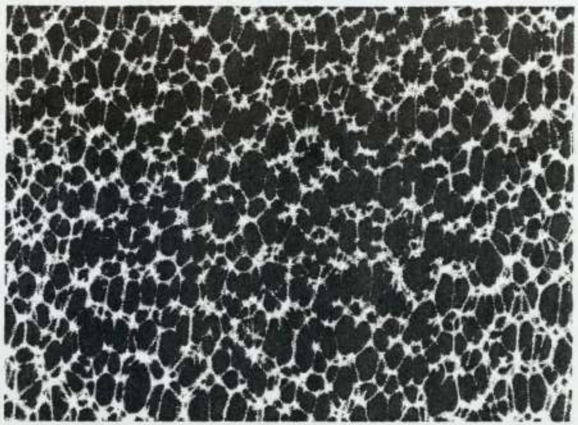
4-6 Open-cells structure

Open-cell foam has cells which are interconnected (picture 2). The foam has little resistance to the passage of liquids and gases.

Picture 2: open-cells structure

4-7 Closed-cells structure

Closed-cell foam has cells which are enclosed by a thin wall of compound (picture 3). The cells act as a barrier to liquids and gases. The water absorption is also low in this sponge.



Picture 3: closed-cells structure

4-8 Rigid urethane foams [17-21]

4-8-1 Preparation of the foam

The rigid urethane foam is made by chemical reactions. The properties of the foam are determined by the reactant, the temperature, catalysis and method for the reaction of the ingredients. There are two principal steps for the reaction. First, polyol and polyisocyanate combine to produce a polyurethane polymer. The polymer is then mixed with catalyst, foaming agent and surfactant.

Different densities can be obtained with rigid urethane foams. For lower density (table 7), the blowing agent added is a non-flammable halocarbon solvent with a boiling point at room temperature such as CCl_3F, CCl_2F_2etc. For higher density than 0.50 g/cm^3 (table 7), some water is used with surfactant and catalyst in place of halocarbon. The water is reacting with the isocyanate group of the polyisocyanate to liberate CO_2. Both reactions occur at room temperature or with a moderate heating. Halocarbon-blown foams have different physical properties than CO_2-blown foams.

Blowing agents	**Lowest density**
Halocarbon	0.20 g/cm^3
CO_2	0.40 g/cm^3

Table 7: Density of rigid urethane foams [17]

4-8-2 Manufacture of rigid urethane foams

There are two ways to make rigid urethane foam in industry: batch-type equipment and continuous and intermittent equipments. The two methods are almost equivalent and the only difference is the capacity of producing the foam. Batch-type equipment is used for low volume. A simple electric drill with propeller type agitator mixes the foam ingredients. It is better to use a formulation where the reaction will start only 30 mins after the mixing in order to leave time to the operator to pour the mix in a container. The system producing urethane foams is shown below (figure 20).

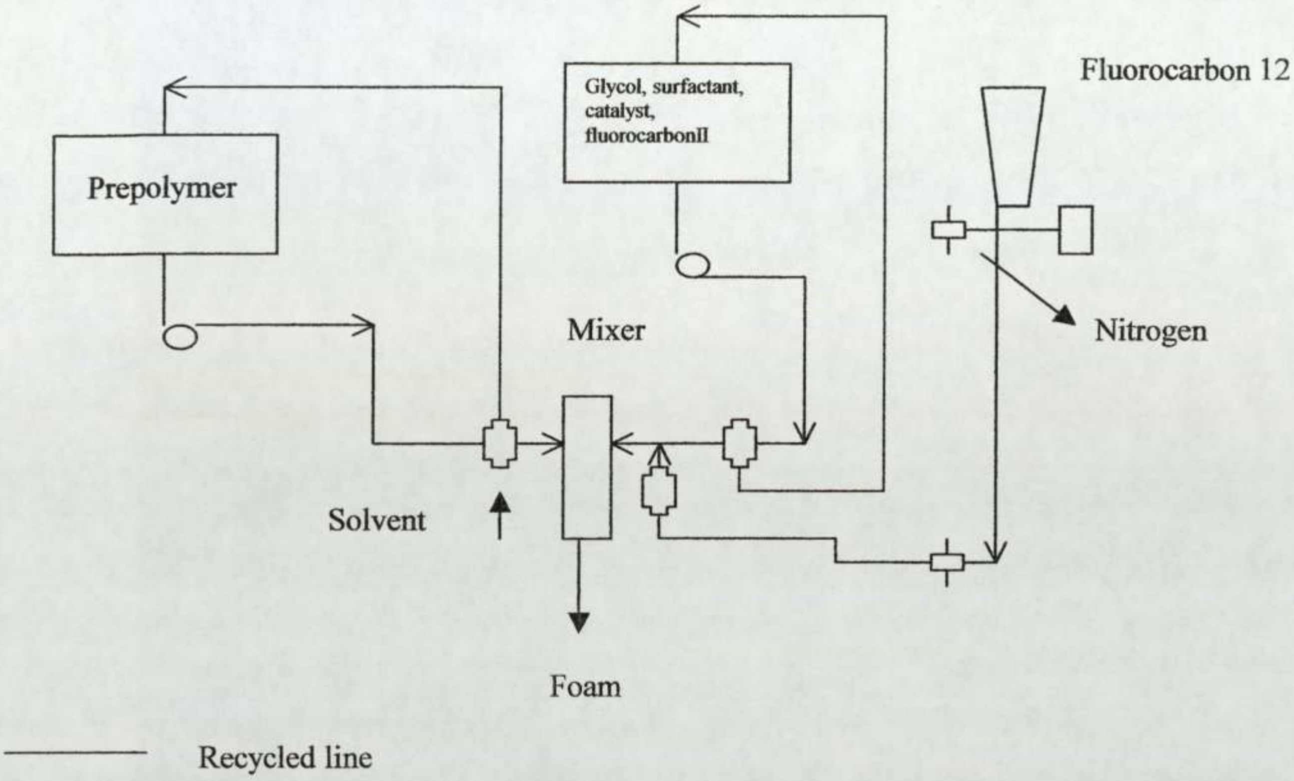


Figure 20: Production of Urethane foam [17]

Rigid urethane foams can be spray applied rapidly to floors, walls, overhead surfaces or onto complicated shapes. There are two different spray equipments. For conventional spray, two separate liquid streams are blending together and are giving a low viscosity liquid which is immediately deposed on target. The mix will react to generate the foam. For froth spaying, the only difference with the first one is that the mix obtained gives a low viscosity froth of shaving cream. It is possible to vary the density of the foam by adjusting the quantity of fluorocarbon. Low density foams have cells elongated in the direction of the rise. Urethane foams have 90% of closed-cells. The density controls mechanical properties such as the compression strength and tensile strength are better with high density. The rigid urethane foam has good thermal conductivity and insulation properties and its dielectric constant increases linearly with the density. Because of its low density and closed-cell structure, the urethane foam has a good flotation property. The applications of urethane foam are shown below in table 8.

Insulation	Roofs, walls, pipe insulation, Aircraft cabins, automobile undercoating, safety helmet, garage door…
Flotation	Ball floats, barges, life rafts, water shoes, surf board…
Art	Amusement park figures, Christmas decorations, mannequins, table lamps…
Packaging	Carboy containers, egg crates, flower containers, explosives, munitions, protecting furniture, radio tube and TV tube packaging, musical instrument cases…

Table 8: Applications of urethane foam [17]

4-9 Polystyrene (PS) foams [17, 22-24]

Polystyrene foams are not adaptable as urethane foams on construction site but they are low cost. Polystyrene foams can be made by extrusion using a PBA or by using expandable PS beads which are normally employed for moulding process but can also be employed for extrusion process.

4-9-1 Extrusion foaming

The first method used is continuous production by injecting a volatile liquid as methyl chloride into the polymer melt. The melt expands by release of pressure at the exit of the extruder and cools rapidly (because of expansion) to produce a low density foam. Logs and planks are produced by this method. Boards are cut from the planks. Extruder dies are used to provide different profiles but the density is not uniform on these shapes.

Another method utilised is to add hexane or a suitable solvent to a pigment which gives a dry powder. The powder obtained is then blended with granular polystyrene and is extruded to produce a low density, fine-celled foam. Extruder has been adapted to continuously inject pentane into the polystyrene melt which contains cell-size controlling additives (such as bicarbonates citrates). Pigments and additives are employed to give different properties to the foam.

4-9-2 Expandable polystyrene manufacture

Expandable polystyrene are used in moulding process. The first method used is to polymerise styrene which contains the foaming agent in an aqueous emulsion. Styrene with foaming agent and catalyst is dispersed in an aqueous medium with agitation. The suspension is heated with agitation for several hours until completely polymerised to a higher molecular weight. Beads are then filtered and washed to remove all polymerisation agents.

Another method is to add hydrocarbon blowing agents to a suspension of polymer and to mix it until the polymer absorbed the blowing agent. Blowing agents used are C_5 – C_7 satured hydrocarbons (pentane, hexane, and pentane). They need to have a boiling point below or at softening point of the polymer. Other solvents can be used such as petroleum or a mixture of diethylether and ethanol.

Another way to produce expandable polystyrene is to bubble ammonia gas through a concentrated solution of polystyrene in ethyl chloride until a paste is obtained. The paste is then dried, shaped and heated to foam.

Polymerisation of styrene can be done by bead polymerisation (see above other methods) or by bulk polymerisation where polymer is cut into granules or cubes. These particles added to foaming agent can be heated and pressurised until the resin absorbed all blowing agents (carbon dioxide and pentane). This method produces foams with very fine pore sizes.

Expandable PS beads can be coloured. The colouring of expandable polystyrene is done by "dry colouring" which consists of coating the unexpandable beads in a drum tumbler with 0.1 % wetting agent and 0.2 % colorant. Five minutes of tumbling are sufficient to provide uniform distribution of the wetting agent but 30 to 60 minutes are necessary to disperse the colorant. Another method is the colouration of expandable polystyrene by using a solution dyeing. The solution and beads are placed in a container and are soaked for 30 to 60 minutes. Beads are then drained, washed with solvents to remove excess of solution and dried at room temperature.

Typical applications of expandable polystyrene foams are insulation board, general moulding, packaging parts, cups etc.

4-9-3 Processes using expandable polystyrene

Expandable PS are used in extrusion and moulding processes.

a- Extrusion

Foamable polystyrene pellets containing an internal blowing agent are used for extruding film, tubes, rods and other profiles. The material is melted in the extruder and forced through a die to cause expansion by releasing the pressure. For sheet, two blowing agent are used. The primary blowing agent is hydrocarbon and the auxiliary blowing agent is a blend of citric acid and sodium bicarbonate. By-products formed are carbon dioxide and sodium citrate. The extrudate products are suitable for food packaging. The hydrocarbon blowing agent provides plasticisation and allows low extrusion temperature (38 °C to 127 °C). The screw of the extruder has a length to diameter (L/D) ratio of 20:1. The barrel of the extruder is short and has a L/D ratio of 16:1. Breaker plates are used too. The use of high temperature at the die prevents the orientation of the foam and gives a rigid product. The density achieved for 204°C to 232 °C is 0.35g/cm^3. The temperature needs to be controlled to avoid volatilisation of the hydrocarbon.

b- Moulding

Different methods are applied for moulding polystyrene foams.

1- Steam chest moulding

Steam is fed to the chest to heat the mould (figure 21) and is also used around the shape of the mould to cause expansion of the beads and to fuse them into a solid mass. Moulds may be made in aluminium but stainless steel is a better material.

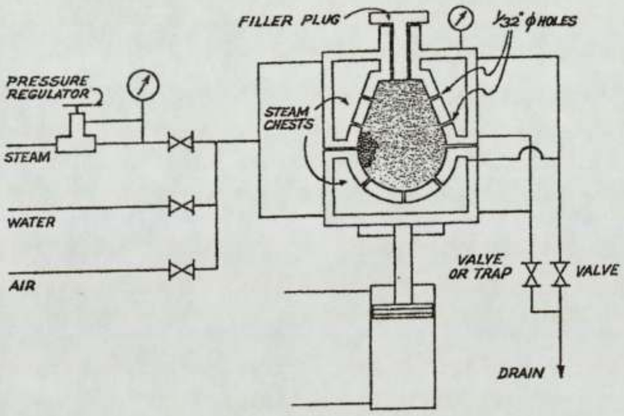


Figure 21: Steam chest moulding [17]

2- Autoclave moulding

Steam is employed too. Perforated shell moulds filled with pre-expandable beads are put in a steam chamber pressurized to 30 psi. Moulding cycles are between 2 and 15 minutes. The mould is then cooled by air or water. It is a costly method.

3- Conducting moulding

Pre-expanded beads of polystyrene are moulded by direct application of heat. This method is only used to mould products with very thin walls. Steam or heat is used to mould the product.

4- Di-electric moulding

Foamable polystyrene can be moulded by radio frequency heating of pre-expanded beads. Water is spread uniformly on the beads. The water heats the pre-expanded beads. Polystyrene beads have low dielectric constant. Moulding cycles are normally 3 seconds and the cooling of product is 30 seconds. The disadvantage of this method is the use of specially treated beads for radio frequency moulding.

5- Injection moulding

Cylindrical granules of expandable polystyrene containing a halocarbon blowing agent are used. Conventional injection moulding machines are used with a high degree of venting. The material is heated in an extruder and is forced through to the mould. When the material expands into the mould, the cooling causes the formation of a skin of high density which gives good insulation to the product. The mould temperature must be controlled: 100 to 150 F. Parts are more expensive by this method because of long moulding cycles.

4-9-4 Applications

Polystyrene foams are non-abrasive, quite deformable and resilient at low temperature. They deteriorate if they are exposed to direct sunlight after a long period. They absorb negligible amounts of water. They have excellent resistance to water absorption and good electrical properties. The applications of polystyrene foams are shown in table 9 below.

Insulation	Ice cream bags and cartons, thermo bottles, fishing boxes, lunch boxes, gaskets (insulating), tank insulation…
Flotation	Rafts, docks, floats, surf boards…
Structural	Sandwich panels, foam boards…
Packaging	Jars and cosmetic containers, food disposable…

Table 9: Applications of polystyrene foams [17]

4-10 Silicone sponges [12, 15]

There are five stages to produce silicone foam: fusion of silicone, compounding of the rubber with catalyst, blowing agents and any fillers, foaming of the compound, curing and post-curing. Silicone sponge is produced by adding a chemical blowing agent to a rubber compound. During vulcanisation, heating causes the blowing agent to decompose, creating bubbles of gas entrapped in the rubber, which form the cells of the sponge. 2,2'-azobisisobutyronitrile (AIBN) was often used with peroxide cure and was liberating nitrogen gases when heated. The structure of the foam was consistent with this technique but toxic by-products were produced. Other blowing agents were tried such as dinitrosopentanethylenetetramine, sulfonhydrazides and azodicarbonamide (ADCA) which are less toxic but the cell structure of the foam was poorer and less consistent. Some companies are actually using microspheres or water to produce foams. Silicone can be produced by using peroxide cure, platinum cure or by combination of silicone resins with polysiloxanes having at least one hydrogen atom on each silicon atom. The hydroxyl groups give self-foaming blends:

$$\sim\text{C-OH} + \text{H-Si}\sim \rightarrow H_2 + \sim\text{Si-O-C}\sim$$

Silicone sponges are produced with the same extrusion machinery and curing equipment used for standard silicone extrusion. General statement on curing and foaming temperature are impossible. It depends on the resin used, the blowing agent, the amount of catalyst and the required density. Foaming and curing must be adapted.

Silicone sponges with a new non-toxic blowing agent needs to have the following characteristics: low compression set, low density, no odour, uniform sponge cell structure, acceptable for food contact application and easy to produce. Search carries on to find a non-toxic blowing agent.

Silicone sponges are used for their low temperature flexibility, their thermal resistance, their UV and ozone resistance and their electrical insulating properties (coming from polysiloxanes). Sponges also provide light weight, cost saving and thermal insulation. Silicone sponges are used for automotive gaskets for sealing compartments, printers, facsimile machines and also for food contact applications including appliance seals for dishwashers and ovens.

Chapter 5:

Foam extrusion

5-1 Extrusion of plastic foams [15, 25-28]

High density foams use CBA which are dissolved in the polymer melt whereas low density foams use liquid or gases blowing agents which are injected into a plasticating extruder. Good instrumentation is necessary to provide adequate control required for the extrusion of foam products. The mix of compound for plastic foam is done in the extruder. Mixing is very important step in any polymer processing. Many ingredients are added to the polymer such as additives, modifiers, fillers, colorants or other polymers. For foam, only polymers, nucleating agents and foaming agents are mixed together. Good distribution and control of foam cells are imperative to obtain the desired foamed product properties. The first step is a good mixing of the foaming agent with the polymer. There are two thermoplastic foam extrusion processes. One creates a high density foam product and the other a low density foam product.

5-1-1 Basic unit operation of foam processes

Polymer system, blowing agent and nucleating agent need to work right together. Processes differ depending on target density, polymer, gas injection and finished product shape. The basic units in the foam extruder are: polymer system feeding, melting / compounding, dynamic sealing, gas injection, distribution, cooling, end homogenisation and die forming.

1- Polymer system feeding

The system feeds a polymer, a stabilizer, a colorant and a nucleating agent. This aim of this step is to disperse the nucleating agent, colorant, additives and to blend the polymer.

2- Melting / compounding

A single screw is used if only melting and light mixing are required whereas twin-screw are used when nucleating agent, colorant have to be dispersed and when more than one polymer need to be blended. The speed of the screw is around 30 to 200 rpm depending of the extrudate. The compound needs to be well mixed before to receive the gas injection.

3- Sealing

The aim of this step is to allow the compounded polymer system to pass but to prevent blow-black of any gases. The elements used may be cascaded discs or special flights. For low gas injection pressure (5 to 20 bars), dynamic seals are introduced in the melting compounding part of the screw.

4- Gas injection

The foaming agent pumping mechanism should provide good volumetric control. Pressure and temperature monitoring are necessary to control the injection.

5- Distribution

Gas is soluble in the polymer system. When the gas is dissolved, the rheology of the material is uniform. Before the gas curve is separated from the material curve. The speed of dissolution is controlled to get the job done with the use of a minimum of energy.

The figure 22 shows how steps 3, 4 and 5 are accomplished.

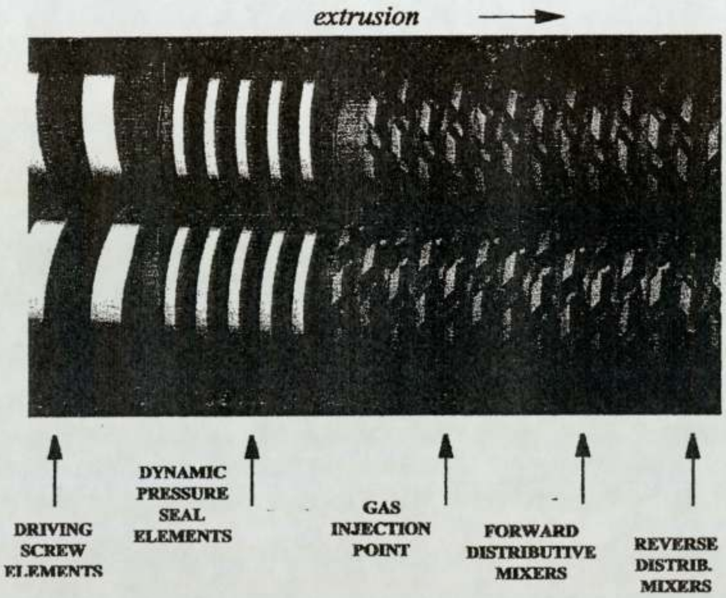


Figure 22: Part 1 of the screw; units for melting/compounding, gas injection and distribution [15]

6- Cooling

When gases are dissolved into the polymer, they function as a Plasticizer. If the viscosity of the melt decreases, the foam density will increase. The melt must be cooled to increase its viscosity in order to be extruded. After gases are mixed, the screw should just cool and forward the melt.

7- Pumping

This step permits to have a powering flow going through the forming die.

The figure 23 shows how steps 6 and 7 are accomplished.

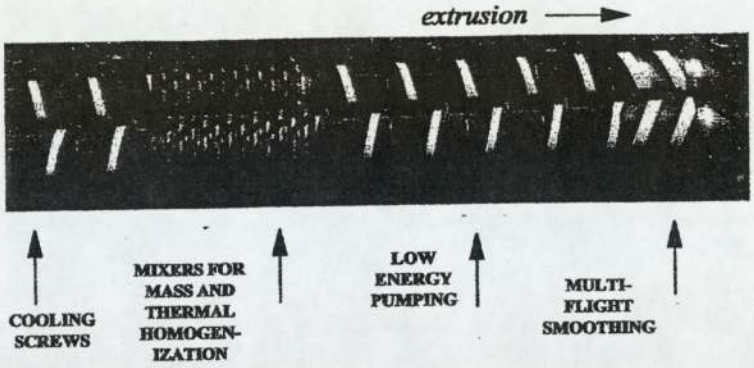


Figure 23: Part 2 of the screw; units for cooling and pumping [15]

8- Die forming

Dies vary with the product type (shapes, density). The temperature of the die must be uniform which helps to keep the nucleating point across the profile section in order to avoid premature nucleation and bubble growth.

5-1-2 Screws

Both single-screw and twin-screw are used to make foam products. Twin-screws transfer mechanical energy like internal mixers through turning two screws or rotors. Single screws are better than twin-screw for two reasons. For a given screw diameter, a single-screw is half price of a twin-screw. Single-screws are also simpler to understand and to maintain whereas twin-screw are greater solids feeding, better dispersive mixing, faster incorporation of blowing agent, better cooling and control temperatures and have more unit operations. Twin-screw are expensive and the heat transfer is limited. The equipment needs to be cooled down more so there are constraints upon the screw speed.

The small width of an extruder gives short transport distance and promotes speed and accuracy for incorporating materials into polymers. Its longitudinal property permits to do sub process in the extruder.

5-1-3 High density foam process

This process uses CBA. PVC is the leading plastic employed but also PE, ABS, PS, PP and other polymers are used to make high density foams. Blowing agents are generally incorporated with the polymer during the pelletizing process. The selection of the CBA depends on the processing temperatures of the polymer. If the decomposition temperature of the CBA is higher than the melt temperature of the polymer, the gas will not be dissolved in the polymer. If the decomposition temperature is lower, the blowing agent will decompose prematurely. The control of the decomposition temperature of the blowing agent and the melt temperature of the polymer is essential. The screw used in this process needs to well mix the compound and the additives. Single and twin screw can be employed. The single screw has a feed throat which is cold because low melt point polymers may stick to the inside surface and barrel zone temperatures which are controlled by monitors. Care must be taken to avoid premature decomposition of the blowing agent but if the temperature is too low, the mix will be poor. A reverse temperature profile on the barrel provides an early melting which improves the mixing. Twin screw is also used for the processing of a wide range of polymers. Screws are designed with feed, compression, first metering, venting, compression and a second metering section. CBA are added at the feed throat of the extruder. The first metering section acts as a dynamic throttle, causing a pressure build up which drives more material. Premature decomposition of blowing agent and loss of gases through feed throat or the venting section have to be avoided. The melt temperature must reach the decomposition of the CBA in the second compression section. The figure 24 represents the units of the extruder.

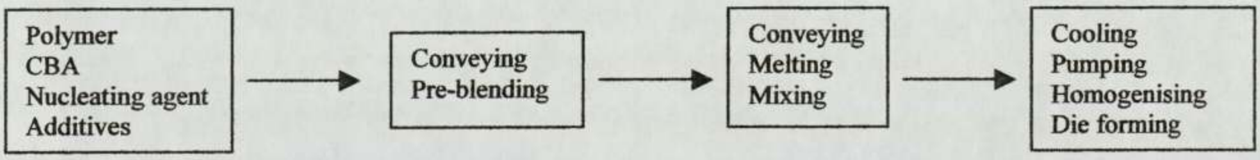


Figure 24: High density foam process with the use of CBA (extrusion) [15]

5-1-4 Low density foam process

Low density foams are made with liquid and gaseous PBA. The lower sponge density achieved is 0.15g/cm^3. Common blowing agents used are HCFC 141b and 142b, hydrocarbons propane, butane and pentane or carbon dioxide. PBA are added in the extruder under high pressure and dissolve in the polymer melt. Two extruders are normally used in tandem. The first one acts as a plasticating extruder and the second as function heat exchanger. They have the same size. Screw design used for solid extrusion is satisfactory for the plasticating extruder. A low temperature is employed at the feeding of the first extruder. Higher temperature than melt temperature in zone 1 provides early melting. Complete melt of the polymer needs to be achieved before reaching the injection port of the blowing agent. The second extruder cools the melt temperature and minimises the energy input to the melt due to mechanical work. The barrel temperature must be below the melt temperature. The screw is different from the first one. There is no need to have a feed section. The polymer melt viscosity is reduced by 50 % after being mixed with PBA (figure 25). The control of the viscosity is important in order to avoid over blowing, cell rupture and collapse of extrudate so low temperature in the barrel zone of the extruder are used. Nucleating agents are also used to provide initial nucleating sites and fine cell structure (such as talc). The figure 26 represents the units of the extruder.

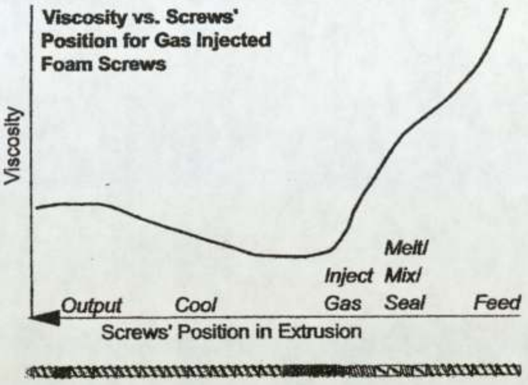


Figure 25: Viscosity curve showing the behaviour of polymer during extrusion [15]

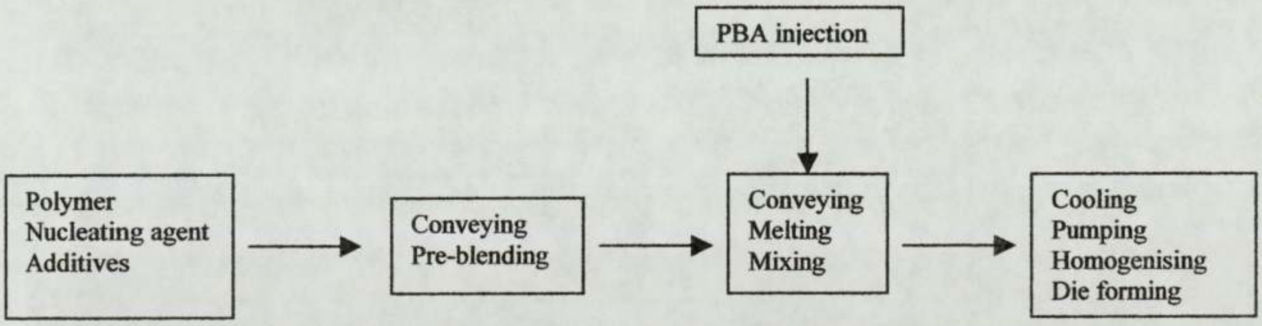


Figure 26: Low density foam process with the use of PBA (extrusion) [15]

5-2 Extrusion of silicone foams [12]

5-2-1 Extruder equipment

It is possible to extrude in continuous lengths different shapes and sizes with silicone rubber. The equipment is similar to the equipment used for organic rubber. (See part 3-3-2 b)

5-2-2 Process design for silicone sponge

CBA is incorporated in the rubber compound by mixing it on a mill. Blowing agents decompose by producing bubbles of gas which form the cells of the sponge prior to curing. The decomposition of blowing agent needs to be closed to the temperature of curing agent. The density of the sponge will vary with the amount of blowing agent, temperature and time. All silicone rubber including fluorosilicone can be sponged. The density of the sponge is

ASTON UNIVERSITY
LIBRARY & INFORMATION SERVICES

0.20g/cm3 with toxic blowing agent and around 0.40 g/cm^3 with a non-toxic blowing agent (so far).

Silicone rubber, curing agent, master batch, additives and blowing agents (CBA) are mixed together using a two-roll mill. The temperature of the mill needs to be lower than 40 °C to avoid loss of curing agent (PDS). When the compound is well mixed, it is rolled and protected by a PET sheet. The material is then ready to be extruded. Small pieces of the compound are fed in the extruder. A single screw is used for silicone. The aim of the screw is to re-mix the compound before cure. The material is pushed through a die. The temperature of the extruder has to be below 50 °C to prevent scorching and loss of curing agent. The extrudate then passes through talc to avoid stickiness on the conveyor belt and is cured through the HAV. The temperature of the HAV zones and the speed of the HAV belt depend on the blowing agent, the curing system and the shape of the product. After cure of the extrudate, a post-cure is done in an oven for 4 hours at 200 °C to remove all volatiles. Post-cure is necessary for material going to be in contact with food. The figure 27 regroups the mix of the compound and the extrusion process. The scheme shows better the difference between the plastic and silicone processing. For plastic, all parts of the process are done in the extruder whereas for silicone the mixing of the ingredient is done before using extrusion equipment.

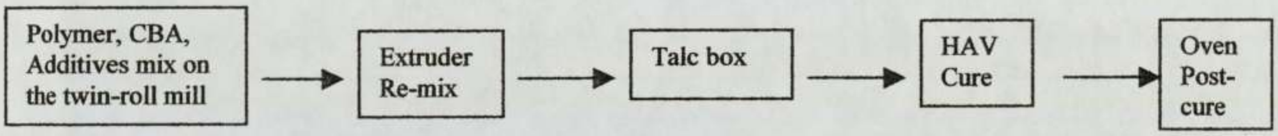


Figure 27: Silicone foam process by extrusion

Chapter 6:

Rubber testing

6-1 Rheometers [29-32]

The measurement of viscoelastic flow behaviour and curing characteristics are required before processing rubber. The viscosity is the resistance to flow of the rubber. The cure rate is measured with a rheometer. Different instruments are used. A mooney viscometer is used for routine quality control. The rotor turns at a constant rate inside a closed cavity containing the test piece so that a shearing action takes place between the flat surfaces of the rotor and the walls of the chamber. The torque required to rotate is monitored. Laboratories are now using curometers which are employed for routine control of fully compound rubbers. There are two types of curometers: the Wallace-Shewbury curometer and the oscillating disc type such as the Monsanto Rheometer. For the oscillating disc type, a bi-conical rotor is embedded in the rubber in a closed cavity. The rotor is oscillated through a small angle and the torque is monitored. One of the platens containing the test piece is oscillated in a rotorless cure meter. The oscillating rheometer was used for this project with the following conditions for silicone rubber. A fixed amount of rubber between two thin Melimex sheets (PET, 36 μm thickness) is placed into two plates for a fixed period of time at a fixed temperature. One plate rotates at a certain angle: 0.50 °. The Monsanto Rheometer MDR 2000 measures the amount of force required to rotate the plate against an applied pressure and gives readout of torque vs. time. There are three different types of behaviour seen forr elastomers. The torque is decreasing after getting to a maximum value: reversion. The torque is increasing continuously: marching. There is no change to the torque: plateau. The preferred result is the "plateau" which proves that all curing agents have reacted (figure 28). Minimum and maximum of the torque, the slope of the curve (cure rate) and the degree of cure are the main values recorded.

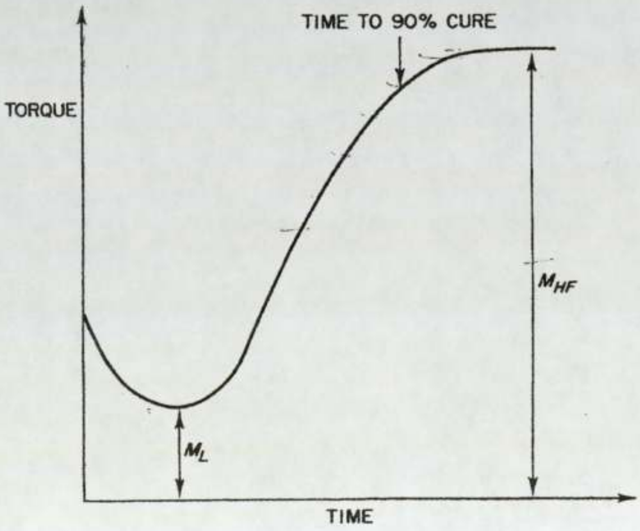


Figure 28: Typical curve obtained with a rheometer

6-2 Tensile strength and elongation [29, 30, 33]

Tensile machine are used to measure the tensile strength, the elongation and the tear of the rubber. Tensile machine are classified as constant rate of traverse. The standard method used is BS903 part A2: 1995 which is describe below.

The tensile stress is a stress applied so as to extend the test piece. It is calculated as the applied force per unit area of the original cross-section of the test length. The tensile strength Ts is the maximum tensile stress recorded in extending the test piece to breaking point.

The elongation is the extension, expressed as a percentage of the test length, produced in the test piece by a tensile stress. The elongation at break Eb is the tensile strain in the test length at break point.

Standard test pieces (dum-bells) are stretched in a tensile-testing machine. Readings of force and elongation are taken during the stretching of the test piece and when it breaks.

The form of Dum-bell is showed in the appendix. Its standard thickness is 2.0 mm ± 0.2 mm and its test length is 20 mm ± 0.5 mm. The other dimensions of the dum-bell (type 2) are showed in the appendix. Minimum of three test pieces are tested. The test of the vulcanised compound is done 16 hours after cure or post-cure. The thickness of the sample is measured with a thickness gauge at the centre of it which is used for the calculation. The test specimen is entered in tensile-testing machine. The tensile machine includes grips and extensometer. Grips (figure 29) are designed to hold the ends of the test piece. Two rollers are utilised for the dumb-bell piece. Talc can be applied at the ends of the dumb-bell to improve the gripping. The rate of traverse should be 500 mm/min. The test is carried at room temperature. Figure 30 shows the curve obtained from the stress and elongation values.

The calculations for the tensile and for the elongation are:

$$Ts = Force / area$$

The unit for the tensile strength is MPa. F is the maximum force recorded in Newtons,

$$Eb = [100 (L_b - L_0)] / L_0$$

The unit of elongation is expressed in percentage, %. L_b is test length at break in mm and L_0 is initial length of the sample in mm

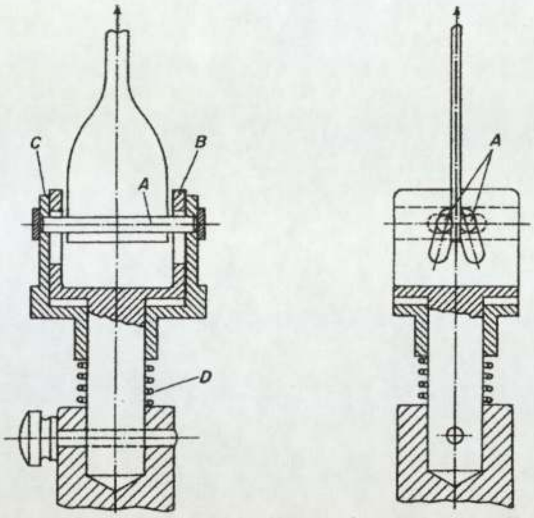


Figure 29: Grips used with Dumbbell specimen in tensile machine [30]

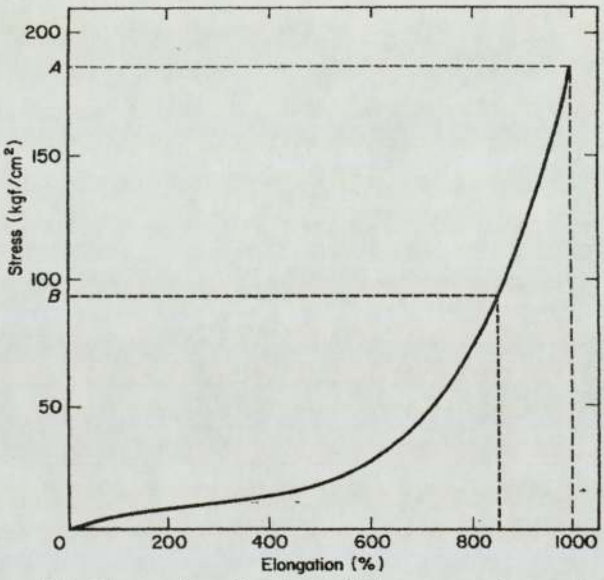


Figure 30: Example of a plot of stress vs. elongation [30]

6-3 Tear strength [29, 30, 34]

The standard method used is ISO 314979: first edition 1979.

The test piece utilised is a crescent test piece with a nick of specified depth. The test measures the force required to propagate a nick already produced in the test piece. The tear force is applied by the tensile-testing machine at a constant rate of 500 mm/min. The nick of the sample can be 0.5 or 1 mm. Five test pieces should be tested. Vulcanised compound have to be tested 16 hours after cure or post-cure. The form of the test piece is showed in the appendix.

The results are calculated as:

$$Ts = F / d$$

The unit for the tear strength is N/mm. F is maximum force in Newtons and d is the thickness in mm of the pieces.

6-4 Density [29, 30, 35, 36]

The standard method used for the determination of density is BS903 part A1: 1996.

The density is the mass of unit volume of the rubber at a stated temperature and is expressed in kg / m^3.

Two methods can be used. Method A is closer to the method used. The mass of test piece in air and in water are determined using an analytical balance equipped with a pan straddle. The mass when immerged in water is less than that the mass in the air. The equipments are an analytical balance accurate at 0.1 mg, a balance pan straddle to support the beaker and a beaker of 250 cm^3. The test piece has smooth surfaces free from crevices or dust and a mass of at least 2.5 g. A minimum of two tests shall be done. The samples have to be tested 16 hours after cure or post-cure at room temperature. The test piece is supported with a filament 25 mm above the straddle and is weighed in the air. The piece is then submerged in distilled water (23 ± 2 °C). Its density is determined by the following calculation:

$$\rho = m_1 / (m_1 - m_2) \ \text{unit kg / m}^3$$

m_1 is the mass of rubber in the air

m_2 is the mass of rubber in water

The density of water is 1kg / m^3 at standard laboratory temperature.

If the use of a sinker is necessary, the calculation is:

$$\rho = m_1 / (m_1 + m_2 - m_3) \ \text{unit kg / m}^3$$

m_3 is the mass of the sinker in water.

6-5 Specific gravity [29, 30]

The relative density is the ratio of the density of a substance to the density of a reference substance (usually water) under conditions that are specified for both substances. The relative density of water is 1 Mg/m^3. The standard method used for S.G is the same as the determination of density: BS903 part A1: 1996.

6-6 Compression set [29, 30, 37]

The standard method used is ASTM D395-89 method B test piece 2, volume 09.01 1990.

The compression set test measures the ability of rubber compounds to retain elastic properties after prolonged action of compression stresses.

The test specimens are compressed and maintained under condition for a specified time and a specified temperature. The test is conducted at elevated temperatures. The form of the test piece is cylindrical disc. For method B, the thickness of the sample is 6.0 ± 0.2 mm and the diameter is 13.0 ± 0.2 mm. The specimens are cut from slab made in the laboratory or moulded. Vulcanised specimens are tested 24 hours after cure or post-cure. The original thickness of the specimens (ti) is measured. The apparatus has two or more flat steel plates. The plates are parallel to each others and spacer bars are put between the plates to ensure the compression thickness. For this method, the thickness of the spacer bars is 4.50 ± 0.01 mm. A force is applied by using screw mechanism for compressing. Suitable time and temperature for compression set are depending upon the conditions of the expected service but general times are 22 and 70 hours. The samples are put in the plate at room temperature and the plate is then put in an oven with desired conditions. When the test is finished, the device is removed from the oven and the test specimens are taking out of the device and cooling at room temperature for 30 minutes. The thickness of the samples (to) is then measured.

The calculation is:

$$Ca = [(to-ti) / to] * 100$$

Ca is the compression set as a percentage of original thickness.

Chapter 7:

Literature survey on blowing agents and silicones sponge

7-1 Knowledge obtained on Primasil sponges

7-1-1 Formulations and process

a- Formulations

Primasil blowing agent used is baking powder: Bex. The formulation was established several years ago and a few variations on this formulation are employed. These are listed in table 10, where pph represents parts per hundred of weight. A list of material is given in the appendix 5 which explain the aim of each material.

Mix 1		Mix 2		Mix 3		Mix 4	
Ingredients	pph	Ingredients	pph	Ingredients	pph	Ingredients	pph
R300/20	100	R-401/20	100	MF25	75	MF25	75
F-celite	25	F-celite	12.5	F-celite	25	F-celite	25
PDS-50	2	PDS-50	2	PDS-50	2	PDS-50	2
Dicup R	0.25	Dicup R	0.25	Dicup R	0.25	Dicup R	0.25
MB01	1.4	Min-u-sil	8.25	901 gum	25	901 gum	25
MB76	0.8	MB37	2	MB01	1	MB01	1.4
Bex	0.63	Bex	0.63	Bex	0.63	MB76	0.8
Cold water	0.35	Cold water	0.35	Cold water	0.35	Bex	0.63
						Cold water	0.35

Table 10: Primasil formulations for silicone sponges made with baking powder

b- Primasil established procedure

A standard procedure is in place for the different sponges. Firstly the material is mixed according to the procedure below and then tested for S.G in the laboratory. After been released from the laboratory, the compound is extruded, the conditions of extrusion depending on the part to be extruded and its dimensions.

- Mixing: general procedure

All powders are placed in an oven at 100 °C for 30 minutes to remove any moisture. A critical amount of water has to be added depending on the amount of baking powder added. If an excess of water is added, the blowing of the sponge can be too great and the cells will not be of uniform size.

Secondly, the Dicup is mixed with some of the base at 60° C in order to dissolve the crystalline Dicup. This is done on a small mill (up to 5kgs). The compound is allowed to cool to room temperature before adding PDS-50, as this material begins curing at temperature below 37 °C.

The bases are then mixed on a bigger mill (up to 50kgs). PDS-50 and the pigments are added to the base. The water and Bex are stirred together in a small container until a paste is formed.

The paste is added on the mill while the compound is being mixed. Finally the powders, F-Celite and Min-u-sil, are added to the mix. The compound is mixed until homogeneous and it is apparent that at the end of the mixing procedure, gas has been generated in the mix, even at temperature of 35 °C.

- Lab testing

Following preparation of the mix, the specific gravity of the material is measured as a standard quality control procedure. No comparison with the last batch of the compound is done. More recently a Rheometer test has been introduced in order to keep a record of the compound cure. From there, the material can be released for extrusion.

- Extrusion

The temperature of the extruder needs to be lower than 40° C. The compound is extruded through a die to obtain the desired shape. The extrudate is passed through talc before being deposited on the moving belt of the hot box. Only one 3 meters hot tunnel is used. The hot box comprises three temperature zones. For Primasil sponge, the temperature of extrusion can vary between 250 to 285 ° C. The temperature is the same all three zones. This process is shown in figure 31.

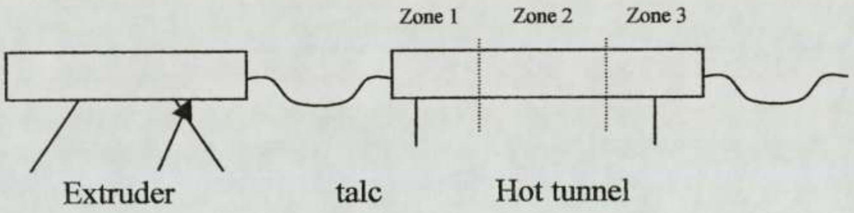


Figure 31: System of extrusion used to produce Primasil sponge with baking powder

The Primasil sponges that are produced by the above scheme are not consistent. Sometimes, the compounds blow well and sometimes not. This variation can be due to the way of mixing differs from one operator to another. Also the baking powder is already reacting when it is mixed with water and a portion of the gases is lost before the paste is added to the mix.

Another cause of the inconsistency can be the hot tunnel. The temperature of each zone varies widely. It is not stable. Just by opening a door of the building can cause the temperature to drop. Also the temperature set on the first indicator is never the same as the temperature measured. The quality of the equipment is very important.

Other possible explanation of the variation can be that the baking powder loses its activity over time. This inorganic blowing agent is difficult to disperse in rubber and may leave undesirable residues in the sponge.

Primasil sponge is a non-toxic product but it is also not very reliable. Another problem appeared by using baking powder as blowing agent. Production and R&D are limited by the shape / sizes of the products. It is very difficult to obtain any samples with a high diameter such as 12mm.

Due to these issues, Primasil is hoping to find a new more robust non-toxic blowing agent and formulation or procedure.

7-2 Information from suppliers

7-2-1 Suppliers of sponge products

The aim of this part is to establish a list of UK suppliers who manufacture sponges with toxic blowing agents. Information on sponge properties has been recorded to understand better the actual market. Primasil company is buying sponge samples from a few suppliers. ADSIL, Jamak, New Metal and Chemical Co and Silicone Engineering are the main suppliers.

a- ADSIL

Advanced Silicone was established in 1987. This company is based in Blackburn and manufactures expanded silicone sponge components which are distributed in Europe, Scandinavia and North America. Their range of sponge products is very wide including cords, tubes, angular sections, profiles, "O" rings, sheet and pads products. The densities of their sponges can vary between 0.16 to 0.55 g / cm^3 and they are produced in a range of different colours. These sponges are resistant to ultraviolet light, to ozone and to oxidizing chemicals. They have very low water absorption. The properties of their main sponge products are listed in the table 11 below.

Properties	**AD 16**	**AD 24**	**AD 33**
Density (g/cm^3)	0.25 ± 0.06	0.40 ± 0.06	0.55 ± 0.06
Elongation %	225	215	245
Compression set 72 hrs@150°C 48 hrs of recovery	15	15	10
Tensile force at break in Newton	65	110	160
Temperature maximum °C of use of the sponge	200	200 - 225	225 - 250
Temperature minimum °C of use of the sponge	- 50	- 50	- 50

Table 11: Properties of ADSIL sponges

Primasil buys some sheet products from ADSIL. The sponge sheets are cut into the shape requested by the customers by Primasil production.

b- JAMAK

Jamak is a company based in Manchester. This company manufactures silicone rubber components: compound, injection and compression mouldings, extrusion, sheeting and silicone sponges, for sale in UK and Europe. They provide the needs for a multitude of markets such as domestic, aerospace, automotive, building, electrical, railway, food industry, general engineering, telecommunications and electronics.

Jamak has a wide range of sponge products with different properties. The densities vary between 0.20 to 0.70 g/cm^3. Their closed cell sponges are available in different colours and can be resistant to high temperature. The sponge is resistant to corona, ultraviolet light, ozone and oxidising chemicals. They have good electrical insulating properties. Typical properties are listed below in the table 12. Jamak is the main supplier of sponge samples for Primasil because of the low density.

	Low density	**Low density**	**Medium density**
Thickness mm	2	6	6
Density g/cm^3	0.25 ± 0.08	0.20 ± 0.08	0.40 ± 0.08
Stress / strain Modulus 40% KPa	60	50	100
Compression set 70hrs@150 °C 25% compression 48 hrs recovery	80 %	85 %	93 %

Table 12: Jamak sponges' properties

Jamak does not use a standard method (ISO or ASTM) to calculate the compression set of their sponges. Compression sets are calculated as the method following. A sample of 100 mm thickness is compressed to 75 mm (25 % compression) and clamped in that position in an oven at 170 °C for 30 minutes. The sample is then removed from the oven and left to cool at room temperature (20 °C) for 30 minutes, then release. The thickness of the sample is measured after 48 hours at room temperature. If the sample is measured at 82 mm after being compressed to 75 mm, it has a recovery of 82 %. If the sample returns to 75 mm, it will have a recovery of 75 %.

According to the ASTM D395, the compression set will be 72 % after calculation and the recovery will be 28 %.

Compression set = [(original thickness – final thickness) / (original thickness – space bar)] X 100

So in fact, their compression set results are low.

c- New Metals and Chemicals Ltd

New Metals and Chemicals Ltd is based in North East London. This company specialises in material technology for the aerospace industry such as silicone foam, composites, ecosphere, metals and inorganic chemicals and fibre composites.

They have a range of silicone foam products available as continuous rolls or in tape form. Their sponge is normally non-toxic, flame resistant and has low water absorption. It has good thermal properties and excellent compression set resistance. Their properties are listed below in the table 13.

Properties	**Value**
Density g/cm3	0.28 – 0.47
Compression set 22hrs@100 ° C	10 %
Flame resistance	HF-1 UL-94 (equivalent)
Water absorption	5 % max
Temperature range	-55 to 205 ° C

Table 13: Properties of HT-800 sponge

d- Silicone Engineering Limited

Silicone engineering has been based in Blackburn since 1959. This company manufactures profiles, sections, sheeting, tubing and cords, gaskets, compound, moulding products in solid and sponge silicone.

They have different grades of sponge: SE 510, SE 515, SE 524 and SE 533. These products are available in different forms and in different colours. They have excellent resistance to ozone, oxidation, ultraviolet light and weathering conditions. Their mechanical properties are listed below in the table 14.

Properties	**SE 515**	**SE524**
Hardness, shore A	13	21
Density, g/cm^3	0.25	0.40
Compression set 22hrs@70 ° C	10 %	10 %
Compression stress/ strain 40 %	90	160
Elongation %	200	250

Table 14: Properties of SE 515 and SE 524 sponges

7-2-2 Suppliers of sponge ingredients

The aim of this part is to list blowing agents with their suppliers and properties. Different suppliers have been contacted. The purpose was to ask for a non-toxic, colourless and odourless blowing agent. The blowing agents were mainly chemical blowing agents. Information on physical blowing agents has been recorded and the use of nucleating agent and microsphere has been pointed out.

The list of suppliers has been recorded and is shown in part 8-3. Some of these companies sent some samples of blowing agents. Trials have been done on them (see section 10 and 11).

7-3 Information on blowing agents

7-3-1 Baking powder

Baking powder is sold by different trademarks such as Londis or Supercook in supermarket. Baking powder is a blend of baking soda (sodium bicarbonate, $NaHCO_3$) and ????and is a safe edible product. The gas obtained after decomposition is carbon dioxide, produced when moisture is added and again when it is heated (100° C). An excess of baking powder in a silicone sponge will produce broken cells and the foam product loses its strength over time giving open-cells.

7-3-2 Nucleating agents

Nucleating agents can be used in two ways. First they can give a high degree of crystallinity to a polymer resulting in improved physical properties such as hardness, elasticity modulus and improved optical properties such as transparency.

Nucleating agents are also used in order to achieve a high cell density. Nucleating agents, such as sodium benzoate, have positive effects contributing to a uniform structure with small cells at low foaming agent concentrations (< 4 wt %). Furthermore, with nucleating agents, the foam density could be increased more gradually when reducing the foaming agent concentration.

7-3-3 Microsphere

The company producing microspheres is Bound minerals and Polymer which is based in Kent. They are suppliers of mineral and polymer raw material for functional and decorative applications, such as resin, thermoplastic, rubber and paint.

The trade name for this product is Expancel®. The microspheres are heat expandable spheres. Each unexpanded sphere contains a droplet of hydrocarbon. When it is exposed to heat, the hydrocarbon evaporates to give bigger sphere (30µm to 80 µm). The expanded sphere is stable at this stage. Expancel® is available in powder form and in masterbatch.

If the product is used alone, the cell structure will be fine and regular. Also microspheres can be added to the compound with some chemical blowing agents. The density obtained is lower with these two components but the cell structure will be less regular.

7-3-4 Bayer blowing agent

Bayer is an international company which is represented on all five continents. They are specialist in chemical products. A sample of Genitron OB was obtained from Bayer.

Genitron OB is a colourless OBSH powder with low decomposition temperature for light foams. It is 4, 4'-oxy-bis (benzene-sulphohydrazide) based blowing agent. It decomposes in applications at temperatures of 140-160 °C. It is a non-staining, odourless and low toxicity blowing agent. Genitron OB can be used in a wide variety of polymers but is specifically utilized in natural and synthetic rubbers (SBR, EPDM, NBR...). It is applied for foam moulding, injection moulding, rotational moulding and extrusion techniques. The amounts of Genitron OB added to a mix vary between 0.5 to 5 % of the total compound. The decomposition products are nitrogen, water and non-volatile residues.

7-3-5 Cylatec blowing agent

Cylatec is a company from United State based in Ohio. This company markets Cylacell which is an endothermic blowing agent.

Cylacell is a white and odourless powder with unlimited shelf-life. This blowing agent is a mixture of sodium and magnesium silicates, sodium borate and chemically bound water. It decomposes at 150 °C without the help of any activators. It is generally used for EPDM, SBR, neoprene, silicone... This blowing agent does not require any post/ cure and is also totally inorganic and azide free. Cylacell is environmentally safe and non combustible. No discolouration or toxic gases should be produced when it is heated.

7-3-6 Douglas blowing agent

Douglas Baker Plastics Ltd was founded in 1979 and is based in the West Midlands. The range of products is wide, including blowing and foaming agents, UV stabilisers, flame retardants, pigments, compounds and other additives. All pigments and additives are supplied in master batch or blend form.

The name of the endothermic blowing agent obtained from Douglas was Bakerblow. It is a stabilised acid / carbonate system in a carrier with 50 % of the active ingredient. It is a non-toxic blowing agent. Its physical form is polymer based, off-white coloured pellets which have a melting point of 130 – 200 °C. The level to use should be around 1 to 3 %. Also Bakerblow is suitable for use in polymers which come into contact with food.

7-3-7 Tramaco blowing agents

Tramaco is a German company based in Pinneberg. This company is a supplier of resins and waxes and is specialist in foaming agent.

There were two samples sent to Primasil: Tracell VMQ 5 / 75 K-S and Tracell NC 135 / 85 S.

Tracell VMQ 5 / 75 K-S is an activated azodicarbonamide bound in silicone oil yellow paste. The blowing agent content in this master batch is 75 %. Tracell VMQ has a decomposition temperature of 150 °C and is an exothermic blowing agent whom decomposes into gases such as N_2, CO, CO_2 and NH_3. It also has a faint odour. Tracell VMQ can be harmful if people inhale the gases in excess.

Tracell NC 135 / 85 S is a modified azodicarbonamide in silicone oil bound. Its form is a white, lumpy paste. The blowing agent content in the master batch is 85 % and its dosage should be around 3 to 5 %. Tracell NC has a decomposition temperature of 135 -190 °C.

7-3-8 Whitchem blowing agents

Whitchem is a sales and marketing company specialising in chemicals and mineral distribution based in Staffordshire. Their product range includes different areas such as building & construction, surface coating, rubber & plastics, textiles and household & personal care.

Whitchem blowing agents are obtained from Uniroyal Chemical. There were five samples sent: Chemisperse AZOK75, Celogen TSH, Celogen AZ*, Celogen 754 and Celogen 780.

Chemisperse AZOK75 has 75 % azodicarbonamide in the formulation and is used as a blowing agent for foaming plastics and rubber. Its form is yellow pellets and its decomposition temperature is above 150 °C. The gases released are N_2, CO_2, CO and NH_2. AZOK75 is considered as a harmful blowing agent.

Celogen TSH is p-toluene sulfonylhydrazide (90%). Its form is a cream-coloured, crystalline powder. THS has a characteristic odour when heated and melts at 100 °C. Its decomposition temperature is 110 °C. THS is considered as a harmful blowing agent.

Celogen AZ* is azodicarbonamide (80%). Its form is a yellow-orange powder. This blowing agent has a characteristic odour when heated and its decomposition temperature is 200-215 °C. AZ* is reported to produce a fine uniform cell structure.

Celogen 754 is a modified azodicarbonamide with a composition of 80% of azodicarbonamide and of 1% of zinc-p-tolyl sulfinate. 754 is a yellow-orange powder and its decomposition temperature is 165-180 °C. The blowing agent has a characteristic odour when heated and is harmful.

Celogen 780 is a modified azodicarbonamide with a composition of 80% of azodicarbonamide and of 5% of zinc oxide. Its form is yellow-orange powder and its decomposition temperature is 140-150 °C. This blowing agent has a characteristic odour when heated and is harmful and highly flammable. 780 has been designed for silicone rubber and does not react with peroxide during cure.

7-3-9 Reedy international blowing agents

Reedy International creates and produces thermoplastic additives for injection and extrusion industries such as foaming and nucleating agents. This company is based in United State.

Three blowing agents were sent to Primasil laboratory: Safoam P, Safoam RIC-FP and Safoam FP.

Safoam P is a medium temperature endothermic chemical nucleating and blowing agent. It is used for injection moulding and extrusion applications for thermoplastics. Its form is a white microencapsulated powder of sodium salts of carbonic and polycarboxylic acids. Safoam P liberates CO_2 at 158 - 183 °C and has a faint odour when heated. This blowing agent produces a closed-cell foam and is FDA approved.

Safoam RIC-FP is a low temperature endothermic chemical nucleating and blowing agent. It has the same composition and characteristics as Safoam P. The only differences are the size of the powder particles which are finer for Safoam RIC-FP and the decomposition temperature which is lower than for Safoam P (140 to 165 °C).

Safoam FP is a fin powder endothermic blowing agent which has the same composition as the two others but produces very fine cells. Also its decomposition temperature is 183 °C.

7-3-10 Wacker blowing agents

Wacker is a German (51%) and French (49%) company which is organised into few groups: Siltronic, Wacker Silicones, Wacker Specialties and Wacker Ceramic. They have a wide range of products in the chemistry and semi-conductor sector such as basic chemicals, biotech materials, fine chemicals, fumed silica, functional polymers etc. Wacker sent its two blowing agents to Primasil laboratory: XTB and MTB. They came from Wacker Silicones and are only used with silicone rubber.

XTB is an endothermic blowing agent in a paste form with no-odour and no-toxic decomposition product. XTB produces closed-cell sponge of density 0.40 to 0.50 g/cm^3 for an amount added of 7 to 10 %. XTB is not food approval. The properties obtained for the sponge are not given. Wacker suggested a formulation for the sponge showed in table 15.

R401/40	100 pph
PDS	1.5 pph
XTB	10 pph

Table 15: XTB sponge formulation (from Wacker)

MTB is also a paste form and a non-toxic and odourless product. MTB produces open-cell sponge with an approximate density of 0.50 g/cm^3 for an added amount of 1.7 %. It has food approval. On a second data sheet showing MTB sponge properties, the result for the density varied and other results for physical properties are given (table 16).

Density g/cm3	0.30 – 0.60
Shore A	8 – 15
Tensile strength N/mm2	0.7 – 1.2
Elongation %	300 – 500
Compression set 72hrs at 23 °C / 50 % compression	<10

Table 16: Properties of MTB sponge (from Wacker)

Also for this blowing agent, Wacker gave a formulation shown in the table 17.

R401/40	100 pph
Lucidol	1.7 pph
PDS	0.50 pph
MTB	1 pph

Table 17: MTB sponge formulation (from Wacker)

7-3-11 Dow Corning blowing agent

Dow Corning was established in 1943 specifically to explore the potential of silicones. It was created as a joint venture between Corning Glass Works (now Corning, Incorporated) and The Dow Chemical Company. It is an international company.

Dow Corning managed to develop a sponge product: Silastic.

Dow Corning sponge technology uses water as a blowing agent. The water becomes steam bubbles when the material is heated. It results in a regular and consistent cell structure.

The characteristics of the sponge are: good resilience, low compression set, environmentally friendly, no unpleasant odour, easily moulded or extruded and food contact approval. The sponges are suitable for extruded sponge profiles, seals and gaskets, moulded sponge parts, sponge sheets…

The curing agent for the sponge formulation is a platinum cure. The Dow Corning sponge compound is supplied in three components: HB-ES 5000 sponge base, AMS-5000 sponge curing agent and AMS-5001 sponge surface modifier. It is also possible to add other bases with the HB-ES 5000 base. The sponge is pigmentable.

Dow Corning gives some information on the process of their sponges. The same equipment as used for the silicone rubber processing is used for extrusion and moulding.

For extrusion, they recommend 210 °C at the entrance of the tunnel. The higher is the cure temperature, the lower is the density of the sponge. The optimum condition depends on the size, the shape and the thickness of the sample but also on the number and the length of curing ovens.

For moulding, the conditions are simple. The temperature needs to be between 200 – 250 °C. The time of cure is 60 seconds per millimetre of wall thickness. It also recommended to apply some talc to smooth the flow of the material in the mould. The preform has to be 50 % of the total volume. Typical properties of Dow Corning sponge are showed in the table 18.

Physical property	**Value**
Specific Gravity	0.37
Density in g/cm^3	0.37
Resilience %	52
Compression deflection (25%) KPa	27.6
Compression set, %set 22hrs@150 °C / 25% / 30 mins rest 22hrs@150 °C / 25% / 24 hrs rest	 16.24 13.1
Compression set, %set 22hrs@100 °C / 50% / 24hrs rest	 5.56
Low temperature brittle, 3mins@-55 °C	No cracks
Water absorption %	1.5

Table 18: Dow Corning sponge properties

7-3-12 Rhodia blowing agent

Rhodia is a world manufacturer of specialty chemicals. Their market touches different areas such as consumer care, food, agrochemicals, pharmaceuticals, automotive, electronics, tyres, fibers, paints and coatings.

The name of Rhodia blowing agent is BA01 which is a non-toxic, water-based chemical product. Its temperature of decomposition is 200 °C. Its shelf-life is three months. Rhodia gave some advice and information on their product. It is possible to use it with two different bases (grade MF40U and MF620U). The formulation is indicated in the table 19.

Base	100 pph
Lucidol	1.27 pph
PDS	0.42 pph
BA01	1 pph

Table 19: Rhodia sponge formulation

A specific technique for the mixing process is advised. First the base has to be mixed with Lucidol on a mill. Then PDS is added to the mix as in method explained later in 9-3-1. Only at the end when the mixture is well mix, BA01 will be added in order to minimise shrinkages. For the extrusion process, a 6 meters hot tunnel is used with 250 °C for the temperature. The speed of the belt needs to be 3m/min. After extrusion, the samples are post-cure for 4 hours at 200 °C. The visual aspect of the sponge is checked as well as its density. A small sample of the extruded part is weighed in air and after in water. The difference gives the value for the density of the sponge. Rhodia laboratory obtained 0.55 g/cm^3 for their samples.

7-3-13 Clariant blowing agents

Alfa Chemicals is the distributor for Clariant blowing agents throughout the UK and Ireland. Clariant is an international company with a wide range of market: textile, pigments & additives, masterbatches and chemicals. Two blowing agents were sent: BIF and BIH.

BIF is based on bicarbonate and citric acid. It is a chemical foaming and nucleating agent powder for foaming of thermoplastic resins. BIF is a white powder, non-toxic, FDA and endothermic blowing agent. Its decomposition temperature starts at 140 °C. This blowing agent is used for extrusion (dosage 0.3 to 1.5 %) and for injection moulding (dosage 0.5 to 2.5 %) of thermoplastics.

BIH is almost the same composition as BIF and is also a white powder, non-toxic, FDA and endothermic blowing agent. Its decomposition temperature starts at 160 °C. BIH is an odourless, colourless chemical and is used for extrusion, for injection and rotating moulding (same dosage as BIF) of thermoplastics.

Chapter 8:

General techniques

A general method has been followed for the preparation, extrusion and the testing of each trial.

A typical formulation is given in table 20.

Ingredients	**Amount**
Base	100 pph
Lucidol	1.27 pph
PDS	0.42 pph
BIH	4 pph
Distilled water	0.50 pph

Table 20: Typical sponge formulation with BIH used for the experiments

8-1 Preparation of a sponge rubber mix

In a typical mixing procedure, the components of the mixture were weighed according to the ratio set out above.

A two-roll mill (2 kg mill, Mattew Johnson & Co Ltd) was used to prepare the mixture. 0.7 kg of base silicone (grade MF40U) was milled for 2 mins the base was removed from the mill and a small quantity of Lucidol was added along the length of the base. The band was after rolled up and put back onto the mill. This technique was repeated until all the Lucidol was added. Lucidol was added in this way to prevent loss of the material. Afterward 5.9g of PDS was added to the compound using the same technique as for Lucidol. At this point, the second half of the base (0.7kg) was added to the first mix until it was homogeneous.

The blowing agent and distilled water were stirred together in a container (white bucket of 5 kg) for a few seconds using a blade. As before, several small additions were made to half of the mix. After all the blowing agent was added, the mix was blended for two minutes. The mixture was taken off of the mill in dolly form and stored in a fridge at 5 °C until needed for trials or processing.

8-2 Tests

The uncured mix was tested in the laboratory to measure the specific gravity and the cure properties by Rheometry.

8-2-1 Specific Gravity: S.G.

The specific gravity is the comparison between the density of the compound and the density of the water. The standard method used for this test is BS903 part A1 method A.

A small amount (2g) of compound was rolled into a ball and was weighed with a Wallace specific gravity balance. The sample was placed on to a pin. The balance was set to zero by using two knurled weights. After, the sample (still on the pin) was placed into the water. A beaker of 300ml with distilled water was placed on plinth and raised until the sample was submerged. The SG was taken off the dial. The result was generally between 1.1 and 1.2.

8-2-2 Rheometer test:

The Monsanto Rheometer MDR 2000 was connecting to a computer and software was controlling the testing of the material.

First all information were entered in the software such as product code, batch number, test time and temperature. A green light on the Rheometer indicated when the temperature requested was achieved. From there, a sample of 4.5 g (between two sheets of thin PET) was placed on bottom platen. By pressing "platens", the test was started; the top platen and safety door came down. The testing light stayed red until the end of the test. The cure behaviour of the material was recorded during all the process: torque vs. time: quality test of the compound.

A typical curve is shown in figure 32.

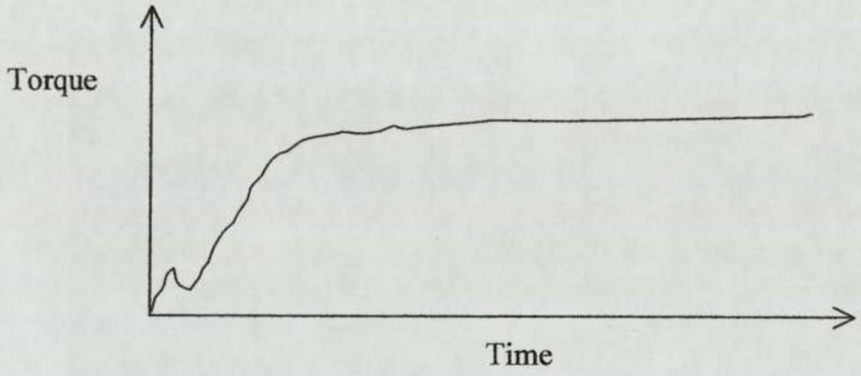


Figure 32: Typical cure behaviour of silicone compound

8-3 Curing process

8-3-1 Method 1: Trials in the oven

The mixing of the material is still the same but a smaller amount of mixture around 200 g was used for each trial.

After the mix, the 200g mixture was formed with the mill in order to get a 5mm sheet. Small squares of 1 by 1 inch were cut. They were cured in the oven at different temperatures and at different times (table 21).

Temperatures	120 to 225 °C
Time	5 to 10 mins

Table 21: Curing conditions for the experimental method 1

The samples were checked on their visual aspect: surface, cell structure and also their density with the formulation: (masse of the sample) / (volume of the sample).

8-3-2 Method 2: extrusion + physical tests

a- Extrusion

The extrusion equipment (figure 33) includes an extruder and two hot boxes. Talc was also applied to the sponge between the end of the extruder and the entrance of the first hot tunnel. The talc was used to enable the sample to move better on the belt and not to stick to it.

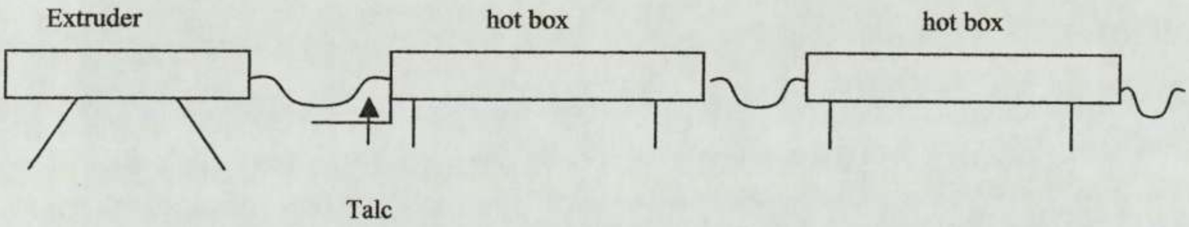


Figure 33: Illustration of the extrusion equipment used in Primasil

A small extruder (up to 1kg) was used for this experiment. The screw and the barrel of extruder must be water cooled because if the temperature is superior at 50 °C, scorching and loss of curing agent will happen. The extruder was fed by small amount of rubber, slowly and continuously. The speed of the extruder depended on the die used and on the speed of the belt in the hot tunnel.

The hot boxes used were a hot air vulcanisation system. Two hot boxes 3 meters in length were used together. There were three zones of temperature for each tunnel. Also the speed of the belt was set to keep the sample inside of the tunnel for four minutes allowing time to blow and to cure correctly. Examples of conditions are given in table 22.

Die	**rpm**	**Belt's speed**	**Temperatures ° C**
Cord 5.2 mm ø	05	2 m/min	170 180 190 // 200 200 210
Cord 6.2 mm ø	10	2 m/min	170 180 190 // 200 200 210
Sheet 5 mm * 1 mm	18	2.5 m/min	170 176 180 // 180 180 175
Strip 2mm thickness	980	1.75 m/min	170 176 180 // 180 180 175

Table 22: Condition of extrusion for the experimental method 2

b- Physical testing

- Density

A formulation was used to calculate the density. The unit of the density is g/cm^3.

$$\text{Density} = (\text{masse of the sample in g}) / (\text{volume of the sample in cm}^3)$$

A sample of extruded sponge was weighed with an analytical balance at ± 0.001 g. The weight of the sample needed to be at least 2.0 g in order to have consistent results. Its thickness (h), length (l) and width (w) was measured with a gauge. From this, the volume of the sponge was calculated:

$V\ (\text{cm}^3) = h\ (\text{cm}) * w\ (\text{cm}) * l\ (\text{cm})$ as also the density with the formulation given above.

- Tensile test and Elongation test

For tensile, elongation and modulus, the standard method used was BS903 part A2 type 2 test piece. To do these tests, a double bell die was used. The sheet die 5mm * 1mm made in extrusion was used for the tests. Five double bells were cut in the length direction of the sheet. The tensometer was connected to a computer and all data were entered: product code, batch number and test setting (table 23). The value for the modulus could be entered at this time. Then a stress / strain graph appeared on the screen of the computer. Values for thickness and width of the sample were requested. The width of the sample was fixed to 4 mm (die, part 7-2) and the thickness was measured with a Mitutoyo gauge. (It should be around 2 mm.) The samples were placed in the Hounsfield tensometer one at a time. The results for the tensile and for the elongation were obtained automatically together for the same test. The results for the tensile strength are given in kPa and for the elongation in %.

Load range	200
Test speed	500
Gauge length	20
Max. extensometer range	1000
Auto-reverse	on

Table 23: Settings for tensile strength and elongation test for silicone sponges made in production

- Tear test

For the tear test, the standard method used was ASTM D62486. The sheet die 5mm * 1mm made in extrusion was used for the tests. The die used for the test was the die C with a nick of 0.5 mm. Three samples were cut from the sheet sample along its length. Only the thickness of the sample was recorded this time which should be around 2mm. The thickness was measured with the Mitutoyo gauge. The tensometer was used for the tear test with different software. All data were entered: product code, batch number, test setting (table 24) and the thickness of the sample. The samples were placed in the Hounsfield tensometer and the stress / strain data recorded. The results are given in N/mm2.

Load range	200
Extension range	500
Test speed	500
Cutter type	C
Auto-reverse	on

Table 24: Settings for tear strength test for silicone sponges made in production

- Compression set test

The standard method used for compression set is ASTM D395-89 method B test piece 2.
A jig with two levels of steel plates was used. Four samples for each trial were tested and were cut from the strip die 2mm* 1 cm. The cured sample tested were rectangular form of 2 * 1.5 cm. The actual thickness of the samples was around 6mm. Washers were used to fix the height of the samples (3mm for 50 % compression or 4.5mm for 25 % compression).
The general conditions used are given in the table 25.

Conditions	compression	Time of rest before measurement
22hrs@150 °C	25 %	30 mins
22hrs@100 °C	50 %	24 hrs
24hrs@ 150 °C	50 %	30 mins
70hrs@150 °C	50 %	30 mins

Table 25: Conditions used to do compression set test with silicone sponges

Chapter 9:

Experimental method 1 (oven trials)

9-1 Experiment on blowing agents

9-1-1 Sodium bicarbonate

a- Baking powder

Several trials were done using the baking powder as blowing agent in the formulation table 10 - mix 3 without adding any master batches (colouration). Experiments were carried out on the fillers, the source of water and the curing agent.

1- Fillers

200 g of mixture were prepared following the method 9-1 with the formulations below in table 26. In these experiments the effect of Celite was investigated.

Ingredients	pph	g	Ingredients	pph	g
MF25U	100	176.63	MF25U	100	193.74
F-celite	10	17.66	F-celite	0	0
PDS-50	2	3.53	PDS-50	2	3.87
Dicup R	0.25	0.44	Dicup R	0.25	0.48
Bex	0.63	1.11	Bex	0.63	1.22
Tap water	0.35	0.62	Tap water	0.35	0.68

Table 26: Primasil formulations, altering the amount of fillers and Bex

The mixing process differed slightly from method 9-1. MF25U was mixed on the mill with the Dicup R at 60 °C. When the mill cooled down, PDS-50 was added as described in method 9-1. The Bex was mixed with the tap water in a container of 1kg capacity and added to the mix in very small amounts.

Method 1 was used to prepare the samples to be tested. The cure temperature of this compound was 200 °C and the time used was 5 minutes. The compound was only checked visually because the cell structure and the sample shape were not regular. Reproducible values of the density could not be obtained and the results shown in the table 27 have a large error. The compounds after cure were expanded more than those obtained by a standard Primasil formulation. It was observed that a greater number of cells were present. By adding less filler, the density of the sponge decreased a little. The cell structure was still not very uniform and fine.

Primasil sponge	0.80 g/cm^3
10 pph of fillers	0.70 g/cm^3
No fillers	0.65 g/cm^3

Table 27: Densities obtained for Primasil formulation with different amount of fillers

2- Source of water

200 g of mixture were prepared following the method 9.1 with the formulations below in table 28.

Ingredients	pph	g	Ingredients	pph	g
MF25U	100	193.74	MF25U	100	193.74
PDS-50	2	3.87	PDS-50	2	3.87
Dicup R	0.25	0.48	Dicup R	0.25	0.48
Bex	0.63	1.22	Bex	0.63	1.22
Tap water	0.35	0.68	Distilled water	0.35	0.68

Table 28: Primasil formulations with different type of water and Bex

Tap water is used in Primasil formulation. The tap water is not pure since it contains minerals. A trial was carried out using distilled water to compare the effect of water with the normal formulation. The mixing process was the same as in the previous experiments and the testing was done following the *method 1*. The temperature and time were 5 minutes at 200 °C. No differences have been found really. The density was around 0.65 g/cm^3. Still the use of distilled water is advised because of the stability of its pH. And by this change the water wouldn't be a factor in the processing of the sponge.

3- Peroxides

PDS-50 (2pph) and Dicup R (0.25 pph) are the peroxides normally used in the cure. A trial has been done by replacing the two peroxides by Lucidol. The aim of this trial was to lower the rate of curing. Lucidol needs 8 minutes at 130° C to cure completely whereas PDS needs 3 minutes and Dicup R 5 minutes. The result was compared to the formulation mix 2 in the table 28 above.

A 200 g mix was made with method 9.1. The formulation used is given in table 29.

Ingredients	pph	g
MF25U	100	195.16
Lucidol	1.5	2.93
Bex	0.63	1.23
Tap water	0.35	0.68

Table 29: Sponge formulations using Lucidol (peroxide) and Bex

Method 1 was used to test the mix. The temperature and time used were 5 minutes at 200 °C. The density did not decrease by changing the nature of curing agents. It was still 0.65 g/cm^3.

b- Sodium bicarbonate as pure chemical

1- The test of the compound was done as *method 1* with the following conditions: 5 minutes at 200 °C and 5 minutes at 175 °C.

Firstly $NaHCO_3$ was used in formulations with different bases (grade: MF25U, MF50U, MF240U, R401/30 and R401/20) and different peroxides. The formulations were prepared with the method 9-1. No water was added in the two first mixes. The amount of $NaHCO_3$ was varied between 1 and 2 pph. Below in the table 30, two general formulations are given for 1 pph of $NaHCO_3$.

Mix 1	**pph**	**g**	**Mix 2**	**pph**	**g**
MF25 U	100	193.52	MF25U	100	196.66
$NaHCO_3$	1	1.94	$NaHCO_3$	1	1.97
Dicup R	0.35	0.68	Dicup R	0.7	1.38
PDS	2	3.87			

Table 30: Sponge formulations using $NaHCO_3$ as blowing agent

After, a variable amount of water was added (0.25 to 0.40 pph) to compare the effect and the expansion of the sponge. The amount of $NaHCO_3$ was varied between 1 and 2 pph. The formulations are given below in the table 31.

Mix 3	**pph**	**g**	**Mix 4**	**pph**	**g**
MF25U	100	193.05	MF25U	100	194.29
$NaHCO_3$	1	1.93	$NaHCO_3$	1	1.94
PDS	2	3.86	PDS	0.42	0.82
Dicup R	0.35	0.68	Lucidol	1.27	2.47
Distilled water	0.25	0.48	Distilled water	0.25	0.49

Table 31: Sponge formulations with distilled water and $NaHCO_3$

None of these formulations gave uniform cell structures or were blowing enough to lower the density of the sponge ($d \approx 0.75\ g/cm^3$).

3- A formulation for sponge was found in the "Polymer Processing" book using $NaHCO_3$. The formulation from the literature is shown in table 32. The goal of using stearic acid is to activate sodium bicarbonate whereas the zinc oxide is used to lower the decomposition temperature of the blowing agent and to transform open cells to closed cells.

Base material (other than silicone)	100 pph
Aid processing / oil	20 pph
Sulphur	2 pph
$NaHCO_3$	15 pph
Stearic acid	8 pph
Zinc oxide	5 pph

Table 32: Formulation given by "polymer processing" book

This formulation was applied to MF25U and R401/30. PDS was used as curing agent instead of sulphur. No water was added first. The formulations were prepared as following. 154.80 g of MF25U was mixed on the mill with 1.86 g of PDS as described in method 9-1. When the mixture was homogenous, the powders (23.22g of $NaHCO_3$, 12.38 g of stearic acid and 7.74 g of zinc oxide) were added together slowly. They were tested with the *method 1* and with the following conditions: 5 minutes at 200°C.

The compound became brown after cure and post-cure. The colour appeared principally on some granules that were not very well mixed. Two other mixes were made to understand the cause of the discolouration; because sodium bicarbonate never produced brown products before. One of the trials was done with only stearic acid and no zinc oxide added. The other one was done with only zinc oxide added to the mix. The formulations are showed below in the table 33.

Mix 1	**pph**	**g**	**Mix 2**	**pph**	**g**
MF25U	100	161.03	MF25U	100	165.02
PDS	1.2	1.93	PDS	1.2	1.98
$NaHCO_3$	15	24.15	$NaHCO_3$	15	24.75
Stearic acid	8	12.88	Zinc oxide	5	8.25

Table 33: Sponge formulations made with $NaHCO_3$, stearic acid or zinc oxide

The results for mix 1 showed that the sponge has a smooth surface but a mix of cells (not uniform). The brown colour appeared on granules not dispersed correctly in the mix.

The results for mix 2 showed that the sponge has a white colour and the cells were uniform. However the surface of the sponge was not smooth at all.

It is believed that the brown colouration is coming from the stearic acid. A few trials were done trying to mix the stearic acid more efficiently with the other powder: using a mortar. Unfortunately, few granules were still showing brown colour after the cure.

Different curing systems were applied: Dicup R, platinum cure. Also the amount of sodium bicarbonate, stearic acid and zinc oxide were changed. But the results were still given a high density ($d \approx 0.70$ g/cm^3) and a brown colour.

When water was added to the formulation to help to mix better the powders together and to decrease the density, the cured compound was coming out of the post-cure very sticky with the platinum cure. No more work was done on this formulation.

c- Mix of sodium bicarbonate and baking powder

The aim of this part was to lower the density of the sponge and to get a better surface and cell structure by adding together some amounts of $NaHCO_3$ and of Bex.

The formulation is given in the table 34.

Ingredients	**pph**	**g**
R401/30	100	193.42
PDS	1.2	2.32
$NaHCO_3$	0.4	0.77
Bex	1.1	2.13
Distilled water	0.7	1.35

Table 34: Sponge formulations made with Wacker base, Bex and $NaHCO_3$

The compound was expanding but it was not enough to lower the density ($d \approx 0.65$ g/cm^3) and the cell structure was still not uniform, no fine cells.

d- Conclusion:

Baking powder as blowing agent did not give good uniform cell structure sponges and the experiments on the fillers, source of water and curing agents did not permit to achieve a lower density than 0.65 g/cm^3. From these experiments and observations on Primasil production, baking powder showed that it is a non-stable chemical in order to get constant results.

Sodium bicarbonate is a non-toxic blowing agent and is blowing but giving only open and non-uniform cells. Pure sodium bicarbonate was used alone or by combination with baking powder but the density of the sponge was still not decreasing. Lower density and uniformity of cells were not achieved by the use of sodium bicarbonate. Further work will be done on baking powder with the extrusion process.

9-1-2 Bayer blowing agent

Bayer blowing agent is Genitron OB, which is 4, 4'-oxy-bis (benzene-sulphohydrazide). It decomposes in applications at temperatures of 140-160 °C.

Different curing agents have been tried: Dicup R, Lucidol + PDS and platinum cure. The amount of Genitron OB has been also varied from 0.5, 5 and 10 % in each formulation. The mixtures have been prepared following the method 9-1. Typical formulations for 0.5 pph of

Genitron OB with different curing agents are shown below in table 35. The compounds were tested with the *method 1* and the following conditions 5 minutes at 200 ˚C.

Mix 1	pph	g	Mix 2	pph	g	Mix 3	pph	g
R401/30	100	195.71	R401/30	100	197.63	R401/30	100	192.31
Lucidol	1.27	2.49	Dicup R	0.70	1.38	MPA 1	2	2.85
PDS-50	0.42	0.82	Genitron OB	0.5	0.99	H68	0.50	0.96
Genitron OB	0.5	0.98				PA2000	1	1.92
						Genitron OB	0.5	0.96

Table 35: Sponge formulations using Genitron OB as blowing agent

For each formulation, the compound did not cure so that the density could not be measured. When more amount of Genitron OB was added to the compound, the cure system was less active. The Rheometer test gave a torque of 1 dNm for 3 minutes at 190 ˚C (Dicup R). It appeared that the Genitron OB hindered the cure system making it of no use for silicone sponge.

9-1-3 Cylatec blowing agent

Cylatec sent one blowing agent to Primasil: Cylacell. It is a mixture of sodium and magnesium silicates, sodium borate and chemically bound water. It decomposes at 150 ˚C without the help of any activators.

Primasil already has a sample of Cylacell ordered few years ago. The curing agent used is Dicup R because of the decomposition temperature of Cylacell (150 ˚C). The temperatures for curing and for blowing need to be almost the same. The amount of Cylacell has been varied from 0.7 to 5 pph.

The formulation was prepared as method 3-1. A typical formulation for 0.7 pph is described: 197.24 g of R401/30 was mixed on the mill with 1.38 g of Dicup R. In order to mix the Dicup R (crystal form), the temperature of the mill was 60 ˚C. When the mix and the mill had returned to room temperature, 1.38 g of Cylacell was added slowly to it.

The compound was curing but it was difficult to obtain enough blowing to get a low density. Their technical department was not able to help or to advice in order to get more blowing and a lower density.

9-1-4 Douglas blowing agent

The blowing agent marketed by Douglas is Bakerblow. It is a stabilised acid / carbonate system in a carrier with 50 % of the active ingredient.

A series of foams with different curing agents: PDS + Lucidol, Dicup R and platinum cure were prepared using Bakerblow. The level of Bakerblow added was 2 pph. The formulations were prepared as in method 9-1 and were tested with *method 1*. The time spent by the sample in the oven and the temperatures of the oven were variables. The conditions were 5 and 10 minutes at 200 and 250 °C. The formulations of the mixes are given in the table 36.

Mix 1	**pph**	**g**	**Mix 2**	**pph**	**g**	**Mix 3**	**pph**	**g**
R401/30	100	192.88	R401/30	100	194.74	R401/30	100	189.57
Lucidol	1.27	2.45	Dicup R	0.70	1.36	MPA 1	2	3.79
PDS-50	0.42	0.81	Cylacell	2	3.89	H68	0.50	0.95
Cylacell	2	3.86				PA2000	1	1.90
						Cylacell	2	3.79

Table 36: sponge formulations using Cylacell as blowing agent

The blowing agent is contained in off-white coloured pellets which have a melting point of 130-200 °C. The pellets containing the blowing agent were not melting for each formulation after a cure of 10 minutes at 200 °C. The compound was then put in an oven at 300 °C but it was burning and the pellets were still not melting.

The supplier sent to Primasil the pure blowing agent without the carrier. The name of the powder is Cenblo MS01. It is an endothermic self-nucleating, blowing agent. Its composition is a stabilised mixture of organic acid and inorganic carbonates. Cenblo MS01 is a white powder with a slight odour. Its melting point is higher to 100 °C.

Trials have been done as usual with using different curing systems: PDS + Lucidol, Dicup R and platinum cure. The amount of Cenblo MS01 added was between 0.50 to 3 pph. With a small amount of blowing agent, the compound was curing but not blowing. With an amount of 3 pph, the compound was blowing but not curing completely. The Rheo test showed a torque of 4.5 which is quite low. Addition of water did not improve the blowing or the curing of the compound. The cured compound was also discoloured (brown).

9-1-5 Tramaco blowing agents

The blowing agent tested from Tramaco was Tracell NC 135 / 85 S. It is a modified azodicarbonamide bound in silicone oil.

Different trials were done using PDS, dicup R and platinum cure. The amount of Tracell NC added varied from 3 to 8 pph. The formulations were prepared with the method 9-1 and were tested following the *method 1*. Typical formulations with 3pph of Tracell are showed in the table 37.

Mix 1	**pph**	**g**	**Mix 2**	**pph**	**g**	**Mix 3**	**pph**	**g**
R401/30	100	191.94	R401/30	100	192.86	R401/30	100	187.79
PDS-50	1.2	2.3	Dicup R	0.70	1.35	MPA 1	2	3.76
Tracell NC	3	5.76	Tracell NC	3	5.79	H68	0.50	0.94
						PA2000	1	1.88
						Tracell NC	3	5.63

Table 37: Sponge formulations using Tracell NC as blowing agent

The compound was curing but not blowing very well with peroxides and with a platinum cure. This was probably caused by the use of silicone oil to make the master batch. The blowing agent does not completely liberate the gases. No more samples have been obtained because Tramaco was not able to confirm if Tracell was safe to use for polymers in contact with food.

9-1-6 Whitchem blowing agents

Trials were done on four blowing agents: Chemisperse AZOK75, Celogen TSH, Celogen AZ* and Celogen 780.

a- Chemisperse AZOK75

AZOK75 is a formulation containing 75 % by weight of azodicarbonamide. Different curing systems have been tried such as Lucidol and Dicup R. The amount of blowing agent was varied between 1 to 5 pph. The compounds were prepared following the method 9-1 and were tested with the *method 1*. The conditions of cure were 5 to 15 minutes at 200 °C. Typical formulations for 1pph of AZOK75 added are indicated in the table 38.

Mix 1	**pph**	**g**	**Mix 2**	**pph**	**g**
MF25U	100	195.69	MF25U	100	196.66
Lucidol	1.2	2.35	Dicup R	0.70	1.38
AZOK75	1	1.96	AZOK75	1	1.97

Table 38: Sponge formulations using AZOK 75 as blowing agent

The compounds did not cure but did blow. Even with increasing the amount of curing agent, the compound was not curing and an orange colour persisted after cure.

b- Celogen TSH

This blowing agent is p-toluene sulfonylhydrazide, 90% pure. Different curing systems were utilized: PDS, Dicup and platinum (table 39). The blowing agent amount was varied between 0.8 to 5 pph.

Mix 1	**pph**	**g**	**Mix 2**	**pph**	**g**	**Mix 3**	**pph**	**g**
MF25U	100	196.08	MF25U	100	196.85	MF25U	100	185.53
PDS-50	1.20	2.35	Dicup R	0.80	1.57	MPA 1	3	5.57
Celogen TSH	0.80	1.57	Celogen TSH	0.80	1.57	H68	1	1.86
						PA2000	3	5.57
						Celogen TSH	0.8	1.48

Table 39: Sponge formulations using Celogen TSH as blowing agent

The compounds were not curing, only blowing. The Rheometer curve registered a torque of 3 dNm: very low or indicating no curing. But the Rheometer curve of the base + curing agents was all right (around 7 dNm for the torque). The presence of the sulphur in the blowing agent had interactions with peroxides.

c- Celogen AZ*

AZ* is a formulation of 80 % azodicarbonamide. Two mixes with the blowing agent and different peroxides have been tried: one with PDS and another one with Dicup R. These were prepared with the method 9-1 and were tested following the *method 1*. The conditions were 5 to 15 minutes at 200 °C. The amount of AZ was 3%. The formulations are showed in the table 40.

Mix 1	**pph**	**g**	**Mix 2**	**pph**	**g**
R401/30	100	191.39	R401/30	100	192.49
PDS-50	1.5	2.87	Dicup R	0.9	1.73
Celogen AZ*	3	5.74	Celogen AZ*	3	5.77

Table 40: Sponge formulations using Celogen AZ* as blowing agent

Again these compounds blew but did not cure. The orange colour persisted. A reaction must have occurred between the blowing and curing agents. Also the decomposition temperature of the blowing agent was quite high (200-215 °C).

d- Celogen 780

780 is a modified azodicarbonamide with a composition of 80% of azodicarbonamide and 5% zinc oxide. This blowing agent has been designed for silicone rubber and does not react with peroxide during cure. Dicup and Varox were suggested as curing agents by the suppliers. Trials have been done with Dicup R. The formulations were prepared with the method 9-1 and tested with the *method 1*. The amount of Dicup R was varied between 0.8 to 1.7 pph and the amount of Celogen 780 was added from 2 to 4 pph. The conditions of testing were 5 and 10 minutes at 200 °C. Typical formulation for 2 pph of Celogen 780 and 0.8 pph of Dicup R added is showed in the table 41.

Mix 1	**pph**	**g**
R401/30	100	194.55
Dicup R	0.8	1.56
780	2	3.89

Table 41: Sponge formulations using Celogen 780 as blowing agent

The Rheometer curve gave a torque of 7 dNm for 2 minutes at 190 °C. The compound was cured and blew. The density was around 0.65 g/cm^3. The sample was not blowing on the direction of the height but on the direction of the width. Also the orange colouration was still present after cure, but the colour was not so strong. The cell structure obtained was fine and uniform.

e- Conclusion

These first blowing agents: Chemisperse AZOK 75, Celogen TSH and Celogen AZ* were blowing but not curing even if the amount of the curing agent was increased. Whereas Celogen 780 gave a cured and blown compound but the density achieved was high: 0.65 g/cm^3.

9-1-7 Reedy blowing agents

Two of blowing agents from Reedy were tested: Safoam P and Safoam RIC-FP.

a- Safoam P

Safoam P is microencapsulated powder of sodium salts of carbonic and polycarboxylic acids. Two curing systems were used for this blowing agent: Dicup R and platinum cure because of the range of Safoam P decomposition temperature: 158 to 183 °C. Peroxides active at high temperatures were needed. The amount of Safoam P used in formulation was between 2 and

10 pph. The formulations were mixed as method 9-1 and tested with the *method 1*. The conditions of the tests were 5 to 10 minutes at 200 °C. Typical formulations for Safoam P at 2 pph are showed in the table 42.

Mix 1	**pph**	**g**	**Mix 2**	**pph**	**g**
MF135U	100	194.55	MF135U	100	191.75
Dicup R	0.8	1.58	MPA1	1	1.92
Safoam P	2	3.89	PA2000	1	1.92
			H68	0.3	0.58
			Safoam P	2	3.84

Table 42: Sponge formulations using Safoam P as blowing agent

The compounds were curing but not blowing. The blowing agent did not generate foam over the range 2-10 %.

b- Safoam RIC-FP

Safoam RIC-FP has the same composition and characteristics as Safoam P. Its decomposition temperature is lower than for Safoam P (140 to 165 °C).

The curing systems used were: PDS + Lucidol, Dicup R, platinum, Varox. The amount of Safoam RIC-FP was varied between 2 to 10 pph. The compound were prepared with the method 9-1 and tested with the *method 1*. The conditions of tested were 5 and 10 minutes at 200 °C. Typical formulations with 2 pph of RIC-FP are showed in tables 43.

Mix 1	**pph**	**g**	**Mix 2**	**pph**	**g**
MF135U	100	194.55	MF135U	100	192.31
Dicup R	0.8	1.56	Varox	2	3.85
Safoam RIC-FP	2	3.89	Safoam RIC-FP	2	3.85

Mix 3	**pph**	**g**	**Mix 4**	**pph**	**g**
MF135U	100	192.88	MF135U	100	191.15
Lucidol	1.27	2.45	MPA1	1	1.91
PDS	0.42	0.81	H68	0.63	1.20
Safoam RIC-FP	2	3.86	PA2000	1	1.91
			Safoam RIC-FP	2	3.82

Tables 43: Sponge formulations using Safoam RIC-FP as blowing agent

Mix 1 to mix 3 did not give good results although curing took place; the blowing was unsatisfactory even with a significant amount of Safoam RIC-FP. The platinum cure was more effective but the cells were very small and not abundant.

Two other trials were done by using in one PDS + Lucidol and in the other a platinum cure. For both of them, some water was added to the mix. The formulations were made following method 9-1 and tested with *method 1*. The conditions were the same as above. The amount of Safoam RIC-FP was varied between 2 and 4 pph. Also the amount of water added was between 0.2 to 0.6 for the peroxide cure and only two drops for the platinum cure. Two formulations are showed below in table 44.

Mix 1	**pph**	**g**	**Mix 2**	**pph**	**g**
MF135U	100	192.51	MF135U	100	191.75
Lucidol	1.27	2.44	MPA1	1	1.92
PDS-50	0.42	0.81	PA2000	1	1.92
Safoam RIC-FP	2	3.85	H68	0.30	0.58
Distilled water	0.20	0.39	Safoam RIC-FP	2	3.84
			Distilled water	2 drops	

Table 44: Sponge formulations made with distilled water and RIC-FP

The compound cured and blew but even with smallest amount of water possible, the blowing agent reacted significantly. The system was not controllable. Although it was not blowing enough before adding water; after putting some water in the mix, the cell structure was not uniform and large cells were obtained.

c- Conclusion

Safoam P blowing agent did not give good results. The compound was curing but not blowing even if a large amount of blowing agent was added. Whereas with Safoam RIC-FP, the compound blew and cured but the density obtained was high 0.70 g/cm^3. By adding water to the formulation, the system was getting difficult to control i.e. large cells were achieved.

9-1-8 Wacker blowing agents

XTB and MTB, Wacker blowing agents, were obtained.

a- XTB

The composition of this blowing agent is not known. The formulation used was that suggested by Wacker (see table 15). The mixture was prepared as described in method 9-1. 179.37 g of base (grade R401/40) was mixed on the mill with 2.69g of PDS-50. When the mix was homogenous, 17.54 g of XTB was added slowly. The compound was tested following *method 1*. The temperatures used for the curing system were from 110 to 250 °C. The cure times for the samples in the oven were 5 and 10 minutes.

The best results were found between 150 and 200 °C (see table 45).

Temperature °C	Time in min	Results
110	10	Not working, no blowing
120	10	Not working, no blowing
130	10	Not working, no blowing
140	10	Not working, no blowing
150	10	No blowing visible but expanding
160	5 10	Expanding only Expanding only
170	5 10	Expanding only Expanding only
180	5 10	Expanding only Expanding only
190	5 10	Expanding only Expanding less
200	5	Expanding a little
225	10	Expanding a little
250	10	Expanding a little

Table 45: Results of the cure of the sponge samples made with XTB, in the oven with different temperatures and times

The bases used for the formulation were R401/20, Wacker grade and the second one R401/30, Wacker grade. Also the amount of XTB has been varied but the results for the XTB sponge were unchanged. No cells are seen on the sample but the sponge compound had expanded. Samples of cured sponges were obtained from Wacker and were found to be similar. The XTB blowing agent produced very fine closed-cells. They are actually invisible without a magnifying glass.

The cure of the formulation has been tested with the Rheometer. The Rheometer curve was alright: Ts2 of 0.16 min and torque of 9.2 dNm for 2 minutes at 130 °C.

b- MTB

The composition of MTB is not given. The formulation used was that suggested by Wacker (see table 17). The formulations were prepared with two different bases (grade R401/30 and R401/40) following method 9-1. The mix composition is given in table 46. Tests were done in the oven as *method 1*. The range of temperature was from 170 to 200 °C and the cure time of the sample in the oven was 5 to 10 minutes.

Mix	Mass in pph	Mass in g
Base	100	193.80
Lucidol	1.70	3.29
PDS-50	0.50	0.97
MTB	1	1.94

Table 46: Sponge formulations using MTB as blowing agent

The compound was blowing and giving open-cell around 190 °C, but the cell structure was not uniform. The cure of the compound has been checked and the density was around 0.60 g/cm^3. The Rheometer curve was alright: Ts2 of 0.19 min and torque of 10 dNm for 2minutes at 130 °C.

The analyses of the MTB blowing agent have been done in Aston University: NMR, GPLC and IR. It appeared that MTB is a blend containing sodium borohydride. Further work has been done by extrusion (part 11-1-2) of materials prepared with this blowing agent.

c- Conclusion

The compound formed with XTB blowing agent cured and expanded but the structure of the sponge was very fine closed-cells, almost invisible. With MTB blowing agent, the compound blew and cured, and had an opened-cell structure. The density achieved was 0.60 g/cm3. Further work will be done by extrusion with MTB.

9-1-9 Dow Corning sponge compound

The compound was ready to be used as purchased. It was purchased in sheet form. The sponge compound was refreshed for two minutes on the mill and prepared as *method1* for testing. The cure temperatures were 220 to 225 °C and the time of cure was 5 to 20 minutes. The samples were post-cured for 2 hours at 200 °C as recommended by Dow. The samples cured and blew and the colour of sponges was clear white and the cell structure was uniform and fine. The density was around 0.36 g/cm^3 for the oven trials. The density given by Dow for this sponge compound was 0.40 g/cm^3. The cure of the compound was checked with the Rheometer. The sponge compound was curing very well with a Ts2 of 0.21 min and a torque of 10.35 dNm for 3 minutes at 190 °C. Further work will be done for this compound by extrusion.

9-1-10 Rhodia blowing agent

The Rhodia blowing agent is BA01, which is a non-toxic, water-based chemical product. The formulation used was suggested by Rhodia (table 19) as was the method of mixing (the same as method 9-1). The amount of BA01 was varied between 1 and 5 pph. The formulations used are showed in table 47 for 1 pph of BA01. The mixtures were prepared following method 9-1 and tested as *method 1* with the following cure conditions: 10 minutes at 200 °C.

Mix	Mass in pph	Mass in g
MF40U	100	194.76
Lucidol	1.27	2.47
PDS-50	0.42	0.82
BA01	1	1.95

Table 47: Sponge formulations using BA01 as blowing agent

Experiments were carried out using other bases such as MF240U, which was added at 20 pph to the normal mix, and MF620U, which was used alone with the formulation. The densities obtained with MF40U or with MF40U + MF240U were around 0.50 g/cm^3. The mix with MF620U produced a lower density sponge 0.40 g/cm^3. But when the sponge was compressed, some air traps were displaced. The increase of blowing agent in the first formulation (table 47) did not lower the density of the sponge.

Another suggestion was to add some Teflon 636N to the formulation to improve the stiffness of the material. 2.31 g was added to the mix in table 47. Teflon made the compound very hard and the density increased to 0.60 g/cm^3.

Work on peroxides was done. The level of Lucidol was decreased to 1 pph but the compound was still curing. Only the MH from the torque was increased (MH_1: 7 to MH_2: 8). When the amount of Lucidol was lower than the amount of PDS, the density was decreased but this was due to the size of the cells (bigger size of cells). The number of cells was not increased. The cells were very open and had big size.

Experiments were carried out on the time and cure of the Rhodia formulation to investigate whether the blowing agent had any influence on these two parameters. The first formulation used was that in table 47 and the second was the same but without any blowing agents. The compounds were prepared with the method 9-1 and tested using the Rheometer. 4.5 g of the mix was placed between two thin sheets of melimex. For the Rheometer test, the temperatures used were: 130, 150, 170 and 190 °C. The time was for all tests 3 minutes. For all temperatures and for the both formulations, the torque obtained was between 7 and 8 dNm. Also for the both formulations, the time TS_2 was decreasing when the temperature was increased. Graphs are showed in the appendix 6.

Conclusion:

Density achieved with Rhodia blowing agent was 0.50 g/cm^3 with the formulation in table 47 using different bases such as MF40U or MF40U + MF240U. The variations of the amount of peroxides did not lower the density of sponge or help to obtain a better closed-cell sponge structure. The last experiment did not show any differences between the Rheometer curves for the normal formulation (table 47) and for the formulation without any blowing agent. It is difficult to distinct two steps of process: one to cure the compound and the other one to blow the compound which may suggest that both steps take place at the same time or also that under pressure the compound did not have the time to blow properly. Further work will be done with the formulation table 47 by extrusion process and in the oven (problem of discolouration).

9-1-11 Clariant blowing agents

Two blowing agents were obtained BIF and BIH.

a- BIF

BIF is based on sodium bicarbonate and citric acid. The amount of BIF used was between 2 and 10 pph. Different curing systems were utilised: PDS, Lucidol + PDS, Dicup R and a platinum cure. The formulations were prepared following the method 9-1 and tested as *method 1* with the following cure conditions: 10 minutes for the cure time and the cure temperature was between 140 and 200 °C. Typical formulations for 2 pph of BIF are shown in tables 48.

Mix 1	**Mass in pph**	**Mass in g**	**Mix 2**	**Mass in pph**	**Mass in g**
MF135U	100	193.80	MF135U	100	194.74
PDS	1.2	2.33	Dicup R	0.7	1.36
BIF	2	3.88	BIF	2	3.89

Mix 3	**Mass in pph**	**Mass in g**	**Mix 4**	**Mass in pph**	**Mass in g**
MF135U	100	192.88	MF135U	100	191.75
Lucidol	1.27	2.45	MPA1	1	1.92
PDS	0.42	0.81	PA2000	1	1.92
BIF	2	3.86	H68	0.30	0.58
			BIF	2	3.94

Tables 48: Sponge formulations using BIF as blowing agent

The samples did not blow for a low amount of BIF. For 10 pph, small cells appeared on the sponge but it was still not expanded significantly.

Some water was added to the mix 3 with the method 9-1 and tested as above. The amount of water employed was between 0.25 and 0.5 pph. The compound was still not blowing sufficiently and when too much water was added, the compound became sticky.

b- BIH

BIH is based on sodium bicarbonate and citric acid and has a decomposition temperature of 160 °C.

The amount of BIH was varied between 2 and 15 %. Different curing systems were used such as Varox, platinum, PDS, Lucidol + PDS and Dicup R. The formulations shown in tables 49 for 2 pph of BIH were prepared as method 9-1 and tested in the oven (*method 1*) with the following cure conditions: 10 minutes for the cure time and the cure temperature was between 140 and 200 °C. Bases used were R401/30 and MF25U.

Mix 1	**Mass in pph**	**Mass in g**	**Mix 2**	**Mass in pph**	**Mass in g**	**Mix 3**	**Mass in pph**	**Mass in g**
Base	100	194.74	Base	100	194.17	Base	100	193.80
Varox	0.70	1.36	Dicup R	1	1.94	PDS	1.2	2.33
BIH	2	3.89	BIH	2	3.88	BIH	2	3.88

Mix 4	**Mass in pph**	**Mass in g**	**Mix 5**	**Mass in pph**	**Mass in g**
Base	100	192.88	Base	100	191.39
Lucidol	1.27	2.45	PA2000	1	1.91
PDS	0.42	0.81	MPA1	1	1.91
BIH	2	3.86	H68	0.50	0.96
			BIH	2	3.83

Tables 49: Sponge formulations using BIH as blowing agent

For low amount of BIH, the compounds did not blow but some small cells appeared when using mix 4 and 5 from table 49. When the amount of BIH was increased to 15 %, the compounds still did not blow sufficiently.

Zinc oxide (0.1 to 0.5 pph) and stearate acid (0.1 to 0.5 pph) were added to the formulation mix 5 table 49 to lower the decomposition temperature of the blowing agent. Unfortunately, it did not improve any of the blowing. The compounds were still expanding very little.

Water was added to the formulation mix 4 table 49. The amount of water added was very small but just enough to permit the reaction to start. If the amount of water was too small, the compound did not blow significantly. Only small cells were formed. If the level of water was too high, the compound was sticky and very difficult to mix on the mill.

The amount of BIH was varied from 2 to 15 % as well the amount of water from 0.3 to 1 pph. The best result obtained was 4 pph BIH the maximum added with 0.50 pph of water. After 4 pph of BIH, the density did not decrease from 0.50 g/cm^3. The amount of water 0.50 pph was the optimum amount for 4 pph of BIH.

Some work was carried out varying the amount of peroxides. The base used was MF25U. First, half of peroxides utilised normally was added to mix (table 50). Then, the amount of BIH was increased in the second mix (table 50) but keeping the same level of peroxides than mix 1. In mix 3 (table 50), only Lucidol was added as peroxides. And finally in mix 4 (table 50), PDS was the only peroxide used. Results and formulations are showed in tables 50. The decrease of peroxides and the increase of the BIH did not improve the value of the density. The use of only PDS gave a non-uniform cell structure.

Mix 1	**pph**	**g**	**Results**	**Mix 2**	**pph**	**g**	**Results**
MF25U	100	190.11	d = 0.51 g/cm^3	MF25U	100	186.22	d = 0.49 g / cm^3
Lucidol	0.50	0.95	Cell structure is uniform but sample is still sticky	Lucidol	0.50	0.93	Presence of bigger cells in the sponge
PDS	0.20	0.38		PDS	0.20	0.37	
BIH	4	7.60		BIH	6	11.17	
Distilled water	0.5	0.95		Distilled water	0.7	1.30	

Mix 3	**pph**	**g**	**Results**	**Mix 4**	**pph**	**g**	**Results**
MF25U	100	189.57	d = 0.52 g/cm^3	MF25U	100	189.57	d = 0.51 g / cm^3
Lucidol	1	1.90	Cell structure is uniform	PDS	1	1.90	Big cells in the sponge
BIH	4	7.58		BIH	4	7.58	
Distilled water	0.5	0.95		Distilled water	0.5	0.95	

Tables 50: Formulations and densities of BIH sponges with distilled water (by method 1)

c- Conclusion

The compound formed with BIF cured but did not blow a lot even if water was added to the formulation. The density was high: 0.80 g/cm^3. The compound made with BIH was cured but did not blow much as with BIF. The use of stearate acid and zinc oxide did not improve the blowing system. The density was still around 0.80 g/cm^3. Water was then added as previous to the BIH formulation. The compound was now blowing. After few works on the amount of peroxides, BIH and water, the best formulation found gave a density of 0.50 g/cm3. The formulation is shown in table 51. This blowing agent is the only one working and gives a low density compared to others; also BIH is not used by other silicone company. It is a new non-toxic blowing agent. More work was done on understand of curing / blowing system and on the different parameters which can change the density (done by Design Experiment) in order to improve the density and the process of sponge product. The BIH compound had been also extruded (part 11-1-5). The results on these two experiments are showed in the next section.

Ingredients	Amount in pph
MF40U	80
MF240U	20
Lucidol	1.27
PDS	0.42
BIH	4
Distilled water	0.5

Table 51: Sponge formulation established with BIH blowing agent (by method 1)

9-1-12 Microspheres

Two trials were carried out to investigate the effect of microspheres on the process: one with only the use of microspheres and the other one with microspheres and BIH blowing agent. The microspheres used were Expancel 092 DU 120 (see section 8-3-3).

The formulations were prepared using the method 9-1. The compositions are given in table 52.

Mix 1	pph	g	Mix 2	pph	g
MF40U	80	152.83	MF40U	80	149.27
MF25U	20	38.21	MF25U	20	37.32
Lucidol	1.27	2.43	Lucidol	1.27	2.37
PDS-50	0.42	0.80	PDS-50	0.42	0.78
Expancel 092 DU 120	3	5.73	Expancel 092 DU 120	1	1.87
			BIH	4	7.46
			Distilled water	0.50	0.93

Table 52: Sponge formulations with Expancel 092 DU 120

The compounds were cured using *method 1* and with the following conditions: 5 minutes at 200 °C. The density obtained with the second mix was lower than with the first mix: 0.45 g/cm^3. The only problem is that after post-cure the sponge became brown. The discolouration is due to the presence of nitrile. The nitrile is the material covering the microspheres. Microspheres do not support the post-cure but in order to use the sponge as food approval, it is important to do the post-cure to get rid of any by-products and volatiles formed. The temperature 200 °C needs to be achieved in order to be sure that all peroxides reacted as well as the blowing agent.

9-2 Experiment on discolouration from Rhodia formulation

The problem was discolouration on Rhodia sponge extruded parts after post-cure. An experiment in the oven as *method 1* was done to understand better the problem and to resolve it. Six mixes were prepared as method 9-1 and tested under identical conditions. The samples were cured for 20 minutes at 200 °C and post-cured for 4 hours at 200 °C. The six mixes were all different. The aim was to find why there was a discolouration by eliminating each ingredient in turn. The formulations are shown in appendix 7 with the results on discolouration before and after post-cure.

Each ingredient had been removed once. First, no blowing agent was added to the formulation. In the second mix, only PDS was used as curing agent. In the third mix, BA01 was replaced by baking powder. In the fourth mix, Lucidol was the only curing agent used. And finally in the fifth mix, the base silicones were changed.

The results showed that the discolouration originated from the use of Lucidol. However if the Lucidol was not used, the sizes of the cell were too big with only PDS. Rhodia had the same problem with their formulation but with a less strong brown colour. A discolouration scale was made to evaluate any discolouration in the future (appendix 8).

Other results by extrusion proved that the discolouration could appear before post-cure if the samples were not cured correctly and if they were cut with metal scissor. Any compounds using Lucidol need to be well cured.

9-3 Experiment on curing / blowing system on BIH formulation

The aim of this series of experiments was to investigate the effects of temperatures and of amounts of BIH on the density of the sample. The density was also measured after cure. The samples were cured for a fixed temperature but with different times of curing.

The formulations were prepared with method 9-1 and tested as *method 1*. The formulation used was that shown in the table 51. Three different bases were utilised MF40U with MF240U and MF25U. The amount of BIH was varied between 4 and 7 pph. The range of temperatures was 160 to 200 °C and the time the sample stayed in the oven was between 90 to 180 seconds.

For MF40U + MF240U, all results had been displayed in two views to be compared. First thing (1) was to do a graph showing density (g/cm^3) vs. time (sec) for each amount of BIH (appendix 9). A curve for each temperature was done for each amount of BIH. For all graphs, the density had a minimum of 0.50 g/cm3. None of the different temperatures was improving the density. The second view (2) was to show the density (g/cm^3) vs. the time (sec) for each temperature. A curve for each amount of BIH was represented for each temperature (appendix 9). Again for all graphs, the density minimum obtained was 0.50 g/cm^3. The increase of the amount of BIH was not improving the density results.

For MF25U, the same ways of looking at the results were done (appendix 9). First view (1) gave the same results as for MF40U + MF240U formulation. The density minimum achieved was 0.50 g/cm^3. The second view (2) proves the same point as before. The density minimum was still 0.50 g/cm^3.

9-4 Design Experiment on BIH formulation

9-4-1 Preparation

The purpose of this design experiment was to understand better the function of the curing and blowing agents. The temperature of the oven and the time the sample spent in the oven were also variables. For the sponge project, the variables were peroxides and BIH for the curing and blowing system. The conditions are shown in the table 53. The response was the density of the sponge sample in g/cm^3.

Ingredients	**Conditions**
Peroxides: Lucidol PDS	 0.7 – 1.4 pph 0.42 – 2 pph
Blowing agent: BIH	3 – 10 pph
Temperature of the oven	120 – 220 °C
Time in the oven	2 – 12 mins

Table 53: Conditions of the design experiment

The variables and the response were entered in the software. Thirty-three experiments were carried out, the data for which are shown in appendix 9. They were prepared with the method 9-1 and tested as *method 1* but with the conditions suggested by the Design Experiment. Each mix has been mixed separately and the individual rheometer curves established. Each compound was cured separately in the oven. The density was measured by using the formulation: d = (masse of sample) / (volume of sample). The results were entered in the software in order to analyse them (appendix 10).

9-4-2 Analysis of Results

The design has been analysed to give the most accurate model, while not introducing errors associated with including factors. The analysis of the design experiment requested some help from outside (appendix 10). From this analysis, the results obtained were given in order to obtain the highest and the lowest density sponges.

For the highest sponge density, the results are given below in the table 54.

Ingredients	Conditions
Peroxides: Lucidol PDS	 0.7 pph 2.0 pph
Blowing agent: BIH	3 pph
Temperature of the oven	120 °C
Time in the oven	2 – 12 mins

Table 54: Formulation and conditions of cure for the highest sponge density, given by the program

The time parameter was unimportant to the "model". The sponge produced would be expected to have a density of approximately 0.84 g/cm^3.

For the lowest sponge density, the results are shown in table 55.

Ingredients	Conditions
Peroxides: Lucidol PDS	 0.7 pph 2.0 pph
Blowing agent: BIH	10 pph
Temperature of the oven	220 °C
Time in the oven	2 – 12 mins

Table 55: Formulation and conditions of cure for the lowest density, given by the program

The time parameter was unimportant to the "model". The Sponge produced would be expected to have a density of approximately 0.39 g/cm^{-3}.

Looking at the results and the information gained from ANOVA, it was clear that the greatest effect on density was caused by blowing agent and temperature, then by the interactions of Lucidol and temperature, PDS with the blowing agent and the blowing agent with temperature.

The 3D graph of the "model" also indicated that outside of the Design Space, it may be possible to have even higher or lower density sponges.

The formulation for the lowest sponge density was tried for extrusion. The results are shown in the next part.

Chapter 10:

Experimental method 2 (extruder trials)

10-1 Work on blowing agents

Baking powder, MTB, Rhodia blowing agent and Dow Corning compound were tried with the extrusion process because they gave good results at the oven trials. BIH being the only blowing agent not used by other competitors and giving a low density at the oven trials was also tested with the extrusion process.

10-1-1 Baking powder

Some trials were done using baking powder as blowing agent in a Primasil formulation (table 10 mix 3 part 8-1-1) without any master batches. Some investigations were carried out on the type of gum and on the source of the baking powder used in Primasil formulations.

a- Gum

Primasil normally utilises 901 gum in their mixes. This gum is made by continuous process so the ratio of polymer is not stable while the ratio of polymer for two other gums: 795 and 759 is controlled for each batch. Two mixes were prepared by production department to compare the use of two gums: 795 and 901. The formulation of the first mix was the same as the one in table 10 mix 3 (section 8.1.1) whereas for the second mix, the only difference was that the 901 gum was replaced by 795 gum. The procedure of mixing and extrusion followed that in 8.1.1(Primasil sponge).

Firstly, the two mixes were tested in the laboratory. The rheometer test showed differences between the two batches. The formulation with 795 gum had a greater cross-link density than the formulation with 901 gum.

The two mixes have then been extruded with the same conditions. The surface of the sponge with 795 gum was not smooth as the surface of the sponge with 901 gum. Another trial should be done with 759 gum because this gum does not have the same composition as the two other gums.

b- Type of baking powder

Primasil purchases baking powder from Londis. Sometimes, the compound made with this blowing agent does not expand when extruded or does not expand enough. One of the suggestions to solve this problem was to try another baking powder hoping that the amount of sodium bicarbonate will be different, i.e. higher and fewer carriers would be required. So Supercook baking powder was tried in production when a mix with Londis baking powder did not work. The formulation is given in table 56 and is the same as mix 3 table 10 (section 8.1.1) except for the origin of the baking powder.

The amount of baking powder was kept constant. A 5 kg mix was prepared and extruded by production department as in 8.1.1.

Ingredients	pph	g
MF25	75	2901.80
F-celite	25	967.27
PDS-50	2	77.38
Dicup R	0.25	9.67
901 gum	25	967.27
MB01	1	38.69
Supercook	0.63	24.38
Cold water	0.35	13.54

Table 56: Primasil sponge formulation using "Supercook" as blowing agent

The die used was a rectangular form of 5mm by 2 mm. The sample expanded satisfactorily. The shape and sizes requested were obtained and the extruded parts were accepted by the customer.

To have more information on these two baking powders, a trial has been done. As above, two 2kgs mixes were done by production in 8.1.1, one mix using Bex from Londis and the other using Supercook's baking powder. The conditions of extrusion were the same as in 8.1.1. A cord die 3.8 mm in diameter was used. The extruded parts were checked visually and the two extruded materials looked identical. The cell structure was the same for both compounds. It would appear that the type of baking powder is not a cause of the problem of expansion.

c- Conclusion

The density of the sponge compounds was checked for each experiment. The density was around 0.70 g/cm^3 even if the origin of the gum or baking powder was changed.

10-1-2 MTB blowing agent

MTB is an endothermic blowing agent sold by Wacker. After preliminary trials done in the oven, a trial was done by extrusion. The compound was prepared as method 9-1 and tested with *method 2*. The formulation used was the one in the table 17 part 8-3-10. Different dies were used: cord 3.8 mm, cord 5.8 mm, cord 7.8 mm and square 9.5 * 9.5 mm. One hot box of 3 meters was utilised. After extrusion, the extruded parts were post-cure for 4 hours at 200 °C. The conditions used for the extrusion equipments are showed in table 57.

1- Cord 3.8 mm	
Rpm of extruder	6.6
Belt temperature, °C	250 in the three zones
Speed of belt	2 m/min
Talc	yes
2- Cord 5.8 mm	
Rpm of extruder	10
Belt temperature, °C	250 in the three zones
Speed of belt	1.7 m/min
Talc	yes
3- square 9.5 * 9.5 mm	
Rpm of extruder	15
Belt temperature, °C	250 in the three zones
Speed of belt	1.7 m/min
Talc	yes
4- square 9.5 * 9.5 mm	
Rpm of extruder	19.5
Belt temperature, °C	220 230 245
Speed of belt	2 m/min
Talc	yes

Table 57: Conditions of extrusion for MTB compound

The samples discoloured when the compound was cut with metal scissors before completely cured (Lucidol in the formulation). The density obtained was calculated with the formulation: (mass of the sample) / (volume of the sample). High results were obtained around 0.60 g /cm^3. When the compound was extruded, the fumes had a distinct quite disagreeable odour.

10-1-3 Dow Corning sponge compound

Dow Corning developed a sponge material using a 9m hot air tunnel. The range of temperatures was separated into three zones: 240 °C, 270 °C and 305 °C and the belt speed of the tunnel was 3.1 m/min. Trials in the oven gave good results (section 10-1-9). Some comparative trials were done by extrusion in Primasil, Dunlop and Dow Corning Company (Cardiff).

a- Primasil trials

The Dow Corning compound was refreshed for 5 minutes on the mill. 2 kgs of compound were used for each trial. The compound was tested as *method 2*, but first only one hot box was utilised. The results of the trials are shown in table 58. The die used was a cord of a diameter 5.2 mm.

Trials	**Temperature of the tunnel °C**	**Speed of the belt m / min**	**Results**
1	240 270 305	3	Not cured
2	240 270 305	1.5	Not cured enough, sample sticky
3	240 270 305	0.2	Burning on the surface
4	300 300 305	2.1	Not cured
5	300 300 305	1.7	Not cured

Table 58: Condition of extrusion for Dow compound with one hot box

The Dow Corning material was very difficult to cure. In another trial, two tunnels were used so that the length of the tunnels was around five meters. The conditions were a little different from *method 2* in that the temperature profiles were changed (Table 59). The samples passed through two different tunnels.

Trials	**Temperature of the tunnel °C**	**Speed of the belt m / min**	**Results**
1	270 270 270 // 280 300 310	1.7	Not curing
2	270 280 290 // 300 300 310	1.5	Not curing
3	290 290 290 // 300 310 310	1.2	Not curing

Table 59: Conditions of extrusion for Dow compound with two hot boxes

The Dow Corning material still did not cure very well even if the sponge compound was passed four times through the hot boxes. The skin of the sample was not smooth and did not stay flat after cure. The speed used was already too slow for production purposes so this parameter could not be changed. It was the same for the temperatures because in order to get a uniform cell structure the temperature needed to be increased slowly. The Primasil hot tunnels can not be heated normally to greater than 300 °C because the life of the heat elements is shorter and the state of the belt deteriorates.

b- Dunlop trial

The second part of the trials was to find a company which own a longer and better belt. Dunlop agreed to help. This company has a five meters hot air tunnel. The control of the temperature zones was very good and stable, and the belt was made from metal mesh. The only problem was that this tunnel is used with 10 kgs capacity extruder. The die brought to Dunlop was a strip form. The control of the extruder speed was very difficult. Beside Dunlop did not look very good to make experimental trials. No good or interesting results were obtained and the compound was not blowing. Dunlop had other customers coming which it was for them the priority.

c- Dow Trial

The last part of the trials was to obtain help from Dow Corning. For commercial reasons, Dow Corning technicians were not authorised to come to Primasil production. So Dow ordered some compounds from Italy and some trials were carried out in their laboratory with the 3 meters hot air tunnel under the supervision of their technicians. The alterations to the conditions (temperature and time) were decided altogether. The temperature of the three zones in the tunnel was changed a few times as was the speed of the belt but the compound still did not cure. Finally, the compound was passed a few times through the tunnel at different temperatures, 240 °C, 280 °C and 350 °C so the samples were passed three times through the hot box, equivalent to 9meters. However the surface of the sample after a while did not stay smooth. The samples had to be put in the oven. The aim of these trials in Dow was to get a cured sample with a uniform cell structure. The die used was a cord form. The results were not conclusive. Dow Corning is now presented their sponge compound in three components and not in just one mix, and is doing conferences on its achieved properties. But no cured samples have been seen so far from them when Primasil asked.

d- Conclusion

The Dow Corning material did not cure very well with the Primasil equipment even if the sponge compound was passed four times through the hot boxes. The skin of the sample was not smooth and did not stay flat after cure and the speed used was too slow for production purposes so this parameter could not be changed. In Dow company, the compound was still not curing with their three meters hot box and their equipment was more efficient than the Primasil one. The aim of these trials in Dow was to get a cured sample with a uniform cell structure but the results were not conclusive.

10-1-4 Rhodia blowing agent

A range of bases (grade MF40U, MF620 and MF40U + MF240U) were used for these trials. The conditions of the experiments were given by Rhodia in order to achieve the best results with their formulation (part 8-3-12). Samples of 1.5 kg were prepared as method 9-1 and tested with the *method 2*.

First, one hot tunnel of three meters length was utilized and the temperature in the three zones was 250 °C as suggested by Rhodia but the speed of the belt was lower than 3 m/min because of the length of the tunnel. Examples of the conditions used are showed in the table 60. The dies used were the same as Wacker trials (part 11-1-2) with some more: cord 6.8 mm, cord 7.8 mm and square of 15 mm by 3 mm.

1- Cord 3.8 mm	
Rpm of the extruder	8.3
Belt temperature, ˚C	250 in the three zones
Speed of belt	2 m/min
Talc	yes
2- Cord 5.8 mm	
Rpm of the extruder	12.25
Belt temperature, ˚C	250 in the three zones
Speed of belt	1.8 m/min
Talc	yes
3- Cord 6.8 mm	
Rpm of the extruder	12.3
Belt temperature, ˚C	250 in the three zones
Speed of belt	1.65 m/min
Talc	yes
4- Cord 7.8 mm	
Rpm of the extruder	1.4
Belt temperature, ˚C	250 in the three zones
Speed of belt	1.4 m/min
Talc	Yes
5- square 9.5 mm by 9.5 mm	
Rpm of the extruder	9.95
Belt temperature, ˚C	250 in the three zones
Speed of belt	1.4 m/min
Talc	Yes
6- rectangular 15 mm by 3 mm	
Rpm of the extruder	13.4
Belt temperature, ˚C	250 in the three zones
Speed of belt	2 m/min
Talc	Yes

Table 60: Conditions of extrusion for Rhodia compound with one hot box

The extruded parts were sticky after extrusion but when higher temperature was applied for the three zones of the tunnel, the compound expanded too much to give uniform cells. The minimum speed of belt used was 1.4 m/min, which is the lower limit of the belt. Under these conditions, the production of the sponge will not be economic. A slight odour was present during extrusion but not as much as Wacker formulation. The compound was curing and blowing, and the cell structure was quite uniform. The density obtained was around 0.55 g/cm^3 for all samples.

Later on, the formulation with MF40U base was tried with two hot tunnels (length now around 6 meters). The 1.5 kg of the compound was prepared as before (method part 9-1) and tested with *method 2*. The aim of this part was to give more time for the sample to cure and to blow and also to avoid any possibilities of discolouration. The die used was a cord 3.8 mm. The conditions are given in table 61. Two different conditions were applied for the temperature.

Cord 3.8mm		
Rpm of the extruder		7
Belt temperature in ° C	1	170 200 200 // 210 210 240
	2	200 210 220 // 230 240 250
Speed of belt		1.5 m/min
Talc		Yes

Table 61: Conditions of extrusion for Rhodia compound with two hot boxes

The density of the samples was still 0.55 g/cm^3 with a uniform cell structure. The use of the two tunnels did not improve the density or solve the problem of discolouration. The discolouration was still sometimes appearing in the middle of the sponge. The discolouration of sponge is discussed in section 10-2.

The Rhodia blowing agent is working; giving a good cell structure and uniform surface. The only problems are the value of the density and the discolouration in the middle of the sponge.

10-1-5 BIH blowing agent

BIH formulations gave the best result in the oven trials compared to the others blowing agents.

a- Trials with the extruder

Trials were done with different bases and with different amount of BIH. The grades of the base used were MF40U, MF40U + MF240U, GP400, R401/20, R420/40 and MF40U + 795 gum. The level of BIH was 4%. This amount was found by the experiment in the oven.

The mixture were prepared with the method 9-1 and tested as *method 2*. The conditions and dies used are recapitulated in the table 62.

1- Cord 3.8 mm	
Rpm of the extruder	3
Belt temperature, ˚C	160 170 200 // 200 210 250 170 180 190 // 200 200 210
Speed of belt	1.8 m/min
Talc	yes
2- Cord 4.2 mm	
Rpm of the extruder	7
Belt temperature, ˚C	195 190 195 // 200 220 230 170 180 190 // 200 200 210
Speed of belt	1.8 m/min
Talc	Yes
3- Cord 6.2 mm	
Rpm of the extruder	10
Belt temperature, ˚C	195 190 195 // 200 220 230 170 180 190 // 200 200 210
Speed of belt	2 m/min
Talc	Yes
4- Sheet 5 mm by 1 mm	
Rpm of the extruder	18
Belt temperature, ˚C	170 176 180 // 180 180 175
Speed of belt	2.5 m/min
Talc	Yes
5- Cord 6.2 mm	
Rpm	0.980
Belt temperature, ˚C	170 176 180 // 180 180 175
Speed of belt	1.75 m/min
Talc	Yes

Table 62: Conditions of extrusion with BIH compound

All these trials were checked by their visual aspect and by their density. Table 63 below showed the results obtained for all different bases. In general, the density had tendency to be around 0.50 ± 0.05 g/cm3. The cell structure for all different bases was uniform as well the surface of the sponge was smooth. A post-cure for 4 hours at 200 ˚C was needed to get rid off all volatiles, stickiness and to be sure that the sponge was completely cured and to use the sponge as FDA.

MF25U	0.53 g/cm^3
MF40U + MF240U (10%)	0.48 g/cm^3
MF40U + MF240U (20%)	0.50 g/cm^3
MF40U	0.50 g/cm^3
MF40U + MF240U (50%)	0.54 g/cm^3
R401/30	0.49 g/cm^3
R420/40	0.49 g/cm^3

Table 63: Density for each BIH sponges made by extrusion in Primasil

b- Variations of the amount of BIH

Another trial done was to look at the variation of the BIH in the formulation. The base used was MF40U + MF240U. The amount of BIH was varied: 2, 4 and 7 pph. The mixtures were prepared as usual and tested with *method 2*. The conditions and results on the density are given in the table 64. One hot tunnel only was used (availability of tunnels difficult). The die cord used was 3.8 mm.

With a low amount of BIH, the density of the sponge was higher (0.62 g/cm^3) as usual (0.50 g/cm^3). The 7 % level of BIH was not improving the density of the sponge which was still 0.52 g/cm^3 and the density of the sponge with 4 % was 0.52 g/cm^3. But this experiment showed that the speed of the belt in the hot tunnel is an important factor for the determination of the sponge density.

Amount of BIH	Density of the sponge	Speed of the belt	Temperature °C
2%	0.70 g/cm3	2 m/min	170-175-180
	0.62g/cm3	1.5 m/min	170-180-180
4%	0.68g/cm3	2 m/min	170-180-180
	0.52g/cm3	1.5 m/min	170-180-180
7%	0.52g/cm3	1.5 m/min	170-180-180

Table 64: Density obtained for compound using different BIH amounts and conditions of extrusion

c- Use of physical blowing agent

The last experiment done to improve the density was the use of a physical blowing agent. Pentane is used for polyurethane foams as a physical blowing agent. The only way to add pentane to silicone compound is to mix some filler with the pentane but the use of fillers increases the density of the sponge and counteracts the improvement provided by the pentane. No decrease of density has been seen with the use of two blowing agents: BIH and pentane + fillers. A density of 0.55-0.60 g/cm^3 has been obtained by using only pentane + fillers as blowing agent.

The problems of employing pentane are its low vaporisation temperature and its odour which involve to keep the temperature of the mix very low and to have very good ventilation along all the process (weight until extrusion).

d- Conclusion

The use of different bases with BIH formulation did not change the value of the sponge density which had tendency to be around 0.50 ± 0.05 g/cm3. The cell structure for all different bases was uniform and the surface of the sponge was smooth. The variation of the amount of

BIH did also not improve the sponge density but this second experiment showed that the speed of the belt in the hot tunnel is an important factor for the determination of the sponge density. The last experiment with BIH formulation using the extruder method was to add a PBA to the formulation in order to lower the sponge density. The use of PBA added more problems to the processing and the work environment.

10-1-6 Nucleating agent

Nucleating agents can be used to obtain a high cell density. By having a higher cell density, the density of the sponge could get lower than 0.50 g/cm^3. 1pph of talc was added to the BIH formulation (table 51). The compound was prepared as method 9-1 and tested with *method 2*. The die used was 3.8 mm and the conditions for extrusion were the same as table 62 (number 1).

The structure of the sponge did not change and the density was still 0.50 g/cm^3 by comparison with the BIH formulation without talc.

10-2 Comparison of cure process equipment

10-2-1 Improvement of process

The aim of this part was to improve the way of process in order to produce low density sponges with small and large sizes. Silicone rubber manufacture involves the use of one "hot box" for sponge materials (part 8-1-1). For all extrusion trials with new formulations, the use of one hot box was not enough to give time for the sample to cure and to expand to low density. Still by slowing the speed of the hot box belt, the compound was not curing enough (semi-cure) or too quick depending on the temperatures used to obtain a low density sponge, and the use of one constant temperature did not give uniform cell structure to the sponge. The use of two hot boxes was imperative to give time for the sample to cure and to blow, and to allow the temperature of the hot boxes to increase gradually in order to have a cured sample and uniform cell structure to the sponge. A series of trials were carried out to establish the optimum curing conditions to obtain low density regular foams. A few problems appeared during trials. The efficiency of the hot boxes was the main problem, because the temperatures at various points inside the hot boxes were different from those indicated. The temperatures varied if the doors of the building were opened or not. There was a gap between the two hot boxes and the entrances and the exits of hot boxes were too large to maintain constant temperature. A moulded sheet of silicone was used to cover the gap between the two hot boxes and metal plates were placed at the entrances and the exits to reduce the gaps. There were no air extractors connected to the hot boxes, so the air inside was not renewed. The concentration of volatiles and fumes increased and varied during processing. The elements of the hot boxes had a white deposit derived from volatile materials generated during processing. Talc was also utilised during trials and was placed before the entrance of the first hot box, which permitted the sponge sample to slide on the belt. Finally, the shape of the die was also a factor. The extrusion die shape should reflect the linear expansion rate of silicone rubber sponge. The BIH sponge blows after the die with an expansion factor of 2, depending on the cure condition and the die geometry needs to be adjusted to compensate for the die swell as the corner areas expand less than straight areas.

It would appear that other competitors are using a 6 meters hot box at least with a speed 3 m/min during cross-linking. The speed used for the trials with Primasil hot boxes was around 1.5 to 2 m/min, depending on the size of the extruded. All the trials in Primasil were carried out with bigger die than Primasil used normally.

To conclude, the trials done in Primasil were not showing very good results. Primasil equipments are old and inefficient. In order to confirm this remark, few trials were done in Italy with new technology. The trials done before (section 11-1-5) shown that a fine tuning between the speed of the belt and the temperatures is important to get a cured and blowing sponge with low density.

10-2-2 Trial in Italy

The aim of this trial was to try better equipment than the one used in Primasil and to compare the final products obtained from this two equipments.

50 kgs of BIH formulation have been prepared by production following the method 9-1. The mix was sent to Colmec (Italy). An extruder made by Colmec up to 20 kgs (appendix 11) was used. The length of the hot air tunnel was 12 meters and air extractors were placed at the entrance, exit and along the tunnel. Three profiles were extruded: cord, strip and tube. The densities of these materials were almost identical to the densities obtained in Primasil (table 65) but their surfaces were smoother and cell structures were more regular with the new equipment (visually). There was no discolouration or stickiness. The temperatures in the tunnel were very precisely controlled and no differences were shown between the temperature set and the temperature indicator. The tunnel was separated into three zones, which could be set to different temperatures. In these three zones, the use of a fan could also be varied, and there was air coming from the bottom of the tunnel and air coming in length direction as shown in figure 34. The tube profile was not realisable with the Primasil formulation and

Primasil equipment whereas with BIH formulation and the new equipment, the tube achieved had a very good shape and the middle hole was empty of rubber.

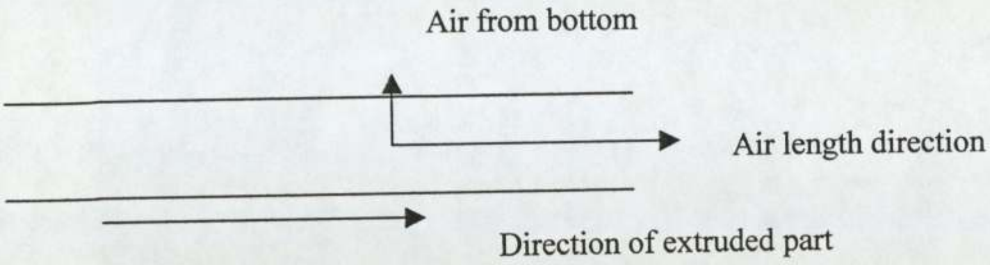


Figure 34: Illustration of fan direction in Colmec HAV

As can be seen in the results (appendix 12), the bottom fan was off for zones 1 and 2. Settings could be changed on temperature, belt speed and fan rpm to achieve best results. The complexity of this hot box was very interesting and proved once more that the conditions of cure were one of the main key (except the formulation) to produce low density sponge. A lot of work on process has to be done to get a low density and cured sponge product.

Extruded part	Density in g/cm3
Cord	0.50
Tube	0.49
Strip	0.45

Table 65: Densities of BIH sponges with new equipments (Colmec)

10-2-3 Infra-red box

The goal of this trial was to try another type of curing equipment. The Dow Corning compound described in section 8-3-11 was used for this experiment. 1 kg of compound was refreshed on the mill for two minutes. Another 1 kg was mixed with 5g of black pigments (C100 Acetylene black). The infra-red box used for curing was obtained from Heraeus. The elements of the box were carbon that allows the heat to diffuse immediately on the materials and curing takes place in few minutes. Two trials were carried with the Infra-red box for each mix. The use of only the infra-red box was not possible because the compound was not curing fast enough and it was not practical to pass through the infra-red box with the uncured compound as shown in figure 35.

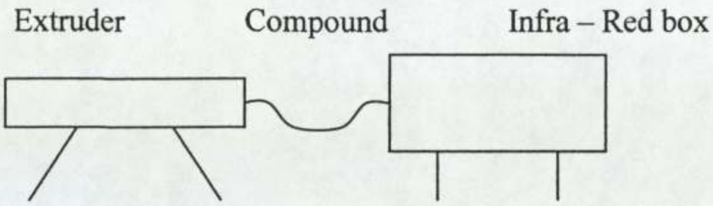


Figure 35: Process for the use of infra-red box (1)

For the second trial, one hot box and the Infra – red box were used together as shown in figure 36 so the compound was curing a little before crossing the Infra-red box. It was easier to pass through the Infra-red box with a semi-cure compound. The white sponge did not give significant result because the compound was not curing completely. The density of the white sample could not be measured, but the black compound cured very well and was post-cure for 4hours at 200 °C. Its density was 0.51g/cm3.

The use of infra-red box is expensive and is not the best approach to cure white sponge products. The carbon elements have more heat effects on dark colour compounds and were not reflected the heat on the white compound.

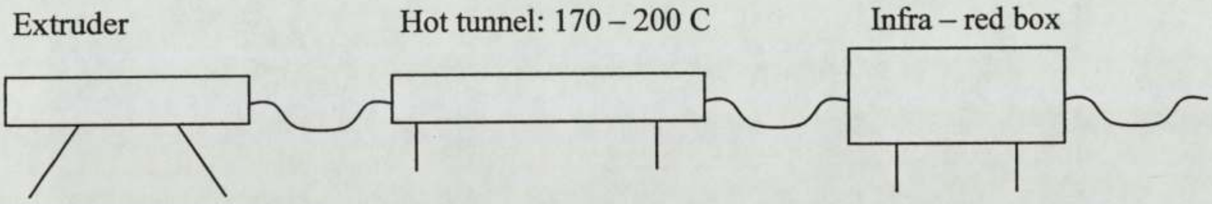


Figure 36: Process for the use of infra-red box (2)

10-3 Conclusion

The goal of this project is to find a non-toxic blowing agent to produce silicone sponges. From this chapter, few aspects have been outline. So far only BIH which is a blowing agent not sold by other competitors has given some correct results by extrusion. The conditions and equipment used to process sponge products are very important and difficult to set. The lower density achieved with BIH is 0.40 g/cm3 in Italy which is still far from 0.20 g/cm3 obtained with a toxic blowing agent. Other competitors such as Rhodia, Dow Corning reached similar density.

Chapter 11:
Properties

Compounds formulated with BIH have been tested on theirs physical properties. These results have been compared to the one obtained by other suppliers which are using a non-toxic blowing agent such as Wacker, Rhodia and Dow Corning and also against the results from the sponges made by toxic blowing agent such as Jamak.

The properties checked on the BIH sponge were mainly its density and cell structure. The density was measured with the formulation method shown in 7-4. Other properties have been verified such as compression set, tensile strength, elongation and tear strength. Results were obtained for BIH formulation using different bases alone or with additives: MF40U + MF240U (20%), GP400, R402/40, MF25U, MF40U + MF240U (50%), MF40U, MF40U + 795 gum, MF40U + RA916.

11-1 Density

The method for measuring the sponge density was a critical point. The method needed to be reliable in order to compare the values obtained with the density of other sponges (competitors). The density formulation part 7-4 was used to calculate the results. The target density was ideally 0.30 g/cm^3. Unfortunately, the density achieved was only in the range 0.40 to 0.50 g/cm^3 with BIH formulations. Several experiments were done to lower the density, such as increasing the amount of BIH (part 11-1-5b), understanding the curing / blowing system (part 10-3 and 10-4) and varying the temperature and time of cure. Different base rubbers and additives were used as shown in table 66 but the results were still in the same range.

Base Die shape	MF40U	MF40U + MF240U	MF40U + RA916	MF40U + 795 gum	MF25U	GP400	R420/40
Cord 3.8mm	0.52	0.50	0.50	0.47	0.51	0.50	0.46
Sheet	0.47	0.51	0.45	0.45	0.47	0.49	0.47
Strip	0.49	0.51	0.50	0.45	0.51	0.54	0.57

Table 66: Density (in g/cm^3) obtained for different extrudates made with BIH formulation

The density obtained by other competitors such as Jamak, ADSIL is around 0.25 g/cm^3 (lowest) but their sponge products are made with toxic blowing agents. The main competitor from Primasil so far is Dow Corning, whose sponge has a density of 0.37 g/cm^3 with a non-toxic blowing agent. The density of BIH sponge may be lowest but more work is required with the use of more efficient equipment, which was seen as a critical parameter in the preparation of sponge.

11-2 Tensile strength, elongation and tear strength.

Several compounds have been tested to measure their tensile strength, elongation and tear behaviour following the method given in part 7-2 and 7-3. The results are shown in tables 67.

Tests / bases	MF25U	MF40U	MF40U + MF240U
Elongation %	553	162	169
Tensile KPa	975	1170	1052
Tear N/mm	4.35	3.48	4.19
Elongation %	229	198	140
Tensile KPa	989	933	813
Tear N/mm		2.81	3.29
Elongation %	287	318	135
Tensile KPa	794	808	833
Tear N/mm	3.80	2.95	3.22
Elongation %			188
Tensile KPa			924
Tear N/mm			3.88
Elongation %			201
Tensile KPa			1026
Tear N/mm			3.94

bases / tests	R420/40	GP400	MF40U + RA916	MF40U + Varox	MF40U + 795 gum	MF40U + talc
Elongation %	184	574	381	150	186	157
Tensile KPa	1450	1167	897	854	789	1229
Tear N/mm	6.13	5.73	3.04	2.91	2.76	

Tables 67: Physical tests on BIH sponges made with different bases

Only two companies provide information on the elongation and the tensile of their sponges: ADSIL (table 11) and Wacker (table 16). The elongation at break of ADSIL sponges is very similar to that found above but the tensile is very weak if it is compared to that shown above. Wacker only provides information on the elongation at break of their sponge. Their results are a little higher (300 to 500) than the values above.

The tests have been carried out to gain more information on the behaviour of the sponges. All results shown in the table 67 with different bases, additives or curing systems gave a wide range of values for each test. The only difference was for GP400. The elongation of this sponge was more important. It may due of the curing system which may react differently in Dow Corning base than one from Rhodia.

None of the competitors have been checked the tear strength. The results obtained were all similar but did not give any quantitative information on the sponge. The sponge was very fragile and broke very easily. The results for the tear strength were very low.

11-3 Compression set

Several trials were done for compression set. First, the die used was very thick (around 5mm for the height) and gave cured sponges of 9 mm height after extrusion. Different tests were done as shown in part 7-6. The results obtained were generally not good because the cells collapsed and the sponge did not return to its original height. The post-cure of the sponge samples was increased from 4 hours to 48 hours at 200 ˚C. The results of further compression set tests (table 68) were better and comparable to other data such as Jamak and Dow Corning sponges. Different bases and additives were tried with BIH blowing agent in order to improve the compression set values. It did not work.

Conditions	**MF25U, set 0.50 g/cm^3**	**MF40U + MF240U, set 0.45 g/cm^3**	**Jamak, set 0.40 g/cm^3**	**Dow Corning 0.37 g/cm^3**
22hrs@100˚C /25%	18%			
22hrs@150 ˚C / 25%	21%	12%		16.24
22hrs@150 ˚C / 50%	45%	4%		
44hrs@150 ˚C / 25%	50%	8%		
70hrs@150 ˚C / 25%	74%		7 %	
22hrs@180 ˚C / 30%		32%		
48hrs@180 ˚C / 30%		77%		

Table 68: Results of compression set for the 5mm die (BIH sponges) compared to Jamak and Dow Corning values

The second test was to use an extrusion die 3 mm thick in order to have samples of 6 mm height (standard height for compression set). Two tests were done as shown in table 69. The results obtained were lower than those obtained in table 68. The post-cure was 4hours or 24 hours at 200 ˚C. The sponge samples only returned a little to their original height.

Conditions	MF40U + MF40U (Primasil), set	MF40U + MF240U (Italy), set
22hrs@150 ˚C, 4 hrs post-cure	83.7 %	82.3 %
22hrs@150 ˚C, 24 hrs post-cure		77.6 %

Table 69: Results of compression set for 3mm die (BIH sponges)

One of the differences between the both tests was the thickness of the dies (3 mm and 5 mm) so that the back pressure in the extruder was different for both dies and the screw speed was slower for the smaller die. The other difference was the cell structure of the sponges. In the 6mm thickness sample, the cells were opened whereas in the 9mm thickness sample, the cells were closed. Closed cell structures give better compression set than opened cells which tend to collapse under compression.

More work is needed in order to understand why the cell structure was different for the same formulation, given that the temperature conditions in the hot tunnel were the same for both experiments.

Jamak report that their samples are left to cool at room temperature for 30 minutes when they are still compressed and release them only after. This technique should be tried for the next trials.

Conclusion

Silicones are synthetic compounds containing silicon, oxygen and organic groups and their chemical properties depend on the silicon-oxygen-silicon skeleton. The organosilicon chemistry's discovery started in 1840 by Dumas and since the development of silicone compounds and its process have been improved by different scientist and companies. The polymer used to prepare silicones is polysiloxanes and its preparation can be done by hydrolysis of chlorosilanes, equilibration of lower siloxanes, ring opening polymerisation and special condensation polymerisation reaction. There are different forms of silicone such as silicone fluids, silicone resins and silicone elastomers (rubber). Silicone elastomers are the one used in this project and have to be vulcanised by peroxides, platinum catalyst and titanium catalyst to form silicone compounds which are processed on the conventional machines of the rubber industry. Additives can also be added during the process. In this project, silicone elastomers have been mixed with a curing system and a blowing agent on a two-roll mill to form a silicone sponge which has been cured by utilising the extrusion equipment (extruder + HAV). The goals requested for this project were to find a non-toxic blowing agent suitable for silicone rubber to make silicone sponges, to extrude different profiles of different sizes (cords, tubes, strips); to achieve a density of 0.25 g/cm^3 and to obtain good compression set recovery. PBA and CBA are utilised to produce foam products. The main type of blowing agent used for silicone rubber is CBA because PBA are generally toxic and require a different process that the one used for silicone compounds. PBA are also very volatile liquid or as gases form. Research literatures on Primasil sponges and other suppliers were done to have a better understanding of the requested properties for silicone foams. The main properties for silicone sponges are density (around 0.25 g/cm^3) and low compression set. Other competitors already accomplished these results but by using toxic blowing agent such as Jamak or ADSIL company. Jamak is one of the main suppliers in UK but the compression set of their sponges is quite high as explained in part 8-2-1b. The only competitors for Primasil in the future are Dow Corning (using "water" blowing agent) which have good results with their sponge products (d = 0.37 g/cm^3 and very low compression set) and Rhodia which has started more research on the use of a non-toxic blowing agent. Experiments have been carried out with different blowing agents in this project. The blowing agents were chemical blowing agents and were tested after been mixed with a silicone base by the oven method (method 1, c.f. part 9-3-1) and if the results were satisfactory (low density and uniform cell structure), the mixing was extruded and cured with HAV such as method 2 (extrusion method, c.f. part 9-3-2). A method was established for the way of mixing the silicone base, curing system and additives which is given in part 9-1 and was utilised for the preparation of each trial. The blowing agents used were baking powder, sodium bicarbonate, Bayer blowing agents, Cylacell, Bakerblow, Tramaco blowing agents, Whitchem blowing agents and Clariant blowing agents. Wacker blowing agents, Rhodia blowing agent and Dow compound were tested to obtain data to compare to the new formulation and to understand more on the process of silicone sponges. The best results were obtained by using BIH blowing agent from Clariant. Trials in the oven showed that the BIH blowing agent with added water gave a foam compound after cure which has a uniform cell structure. After few works on the amount of peroxides, BIH and water, the best formulation obtained gave a density of 0.50 g/cm3. The formulation is shown in table 51 – part 10-1-11. This blowing agent is the only one working from the ones above and gives a low density; also BIH is not used by other silicone company. It is a new non-toxic blowing agent. Trials with the extruder and the HAV for BIH formulation were carried out. It is proved on several trials that the compound is expanding at each use and can give bigger size of extruded parts than the existing Primasil formulation. The aim of the experiment with BIH formulation using the extrusion method was to obtain density lower than 0.50 g/cm^3. The utilisation of different bases with BIH formulation did not change the value of the sponge density which had tendency to be around 0.50 ± 0.05 g/cm3 as for the oven trials. The cell structure for all different bases was uniform and the surface of the sponge was smooth. The variation of the amount of BIH did also not improve the sponge density but this second experiment showed that the speed of the belt in the hot tunnel is an important factor for the determination of the sponge density. By working on the conditions of the extrusion, closed-cell structure and smooth surface can be reached. The last experiment with BIH formulation was to add a PBA to the formulation in order to lower the sponge density. The density obtained was around 0.60 g/cm^3. The use of PBA added more problems to the processing and the work environment. The trials done in Primasil were not showing very good results because Primasil equipments are old and inefficient. In order to confirm this remark, few trials were done in Italy with new technology. The densities of the materials were almost identical to the densities obtained in Primasil but their surfaces were smoother and cell structures were more regular with the Italy equipment (visually). The lower density achieved with BIH in Italy was 0.40 g/cm^3. The temperatures in the tunnel were very precisely controlled and no differences were shown between the temperature set and the temperature indicator. Talc has to be used to permit the sample to move on the belt of the hot air tunnel. Mesh metal belt utilised in Italy leaves the hot air to get around all the samples where the belt used in Primasil does not. The use of fan in Italy also improved the cure and the blow of the sponge. Samples were not sticky after cure. The length of the hot air tunnel is critical too. It needs to be at least 6 meters to permit a good cure and blow of the sample. Any sponge profiles can be made with good extrusion equipment. Tubes were made in Italy during the trials whereas in Primasil, the walls of the tube were sticky together in the middle. The conditions of cure are one of the main key (except the formulation) to produce low density sponge. A lot of work on process has to be done to get a low density and cured sponge product. The conditions and equipment used to process sponge products are very important and difficult to set.

Compounds formulated with BIH have been tested on theirs physical properties. These results have been compared to the one obtained by other suppliers which are using a non-toxic blowing agent such as Wacker, Rhodia and Dow Corning and also against the results from the sponges made by toxic blowing agent such as Jamak. The main properties checked were density and compression set of the silicone sponge. The target density was ideally 0.30 g/cm^3. Unfortunately, the density achieved was only in the range 0.40 to 0.50 g/cm^3 with BIH formulations. Several experiments were done to lower the density but they were unsuccessful. The density obtained by other competitors such as Jamak, ADSIL is around 0.25 g/cm^3 (lowest) but their sponge products are made with toxic blowing agents. The main competitor from Primasil so far is Dow Corning, whose sponge has a density of 0.37 g/cm^3 with a non-toxic blowing agent. With chemical blowing agent, the literature shows that the density of sponge can not be lower than 0.50 g/cm^3 so the density limit can maybe lower a little but not enough to get 0.25 g/cm^3. The other property to establish is the compression set. It is important to use the conditions given by Dow Corning to start because the conditions are not too hard for the sponge (22hrs@150 °C / 25 % compression). Two compression set tests were carried out using two different dies, different additives and silicones bases in the BIH formulation. The results obtained for the compression set were high when the cell structure of the sponge was mainly open-cell and low when the cell structure of sponge was mainly closed-cell. Closed cell structures give better compression set than opened cells which tend to collapse under compression.

More work is needed to improve the compression set of the BIH sponge. It may be interesting also to use Jamak technique because Jamak leave their samples cooling at room temperature after the test for 30 minutes still in the jig and then release them. The samples are measured after 24 hours.

In conclusion, Primasil has a new sponge formulation made with a non-toxic, colourless and odourless blowing agent. This blowing agent is also FDA approved. In order to use the sponge compound for food contact products, a post-cure of 4 hours at 200 °C is necessary as to ensure complete cure of the sponge. This formulation is working each time so it can replace the old Primasil formulation but to compete against other suppliers more efficiently, more work has to be done on the sponge properties and processing.

The cost of Primasil formulation is £ 3.00 per kg and for BIH formulation, £ 4.80 per kg without using any pigments for both. As said before Primasil formulation is not working every times which means that costs and times are wasted in the manufacture and processing of this formulation whereas with BIH formulation the compound is curing and blowing each time. The difference of £ 1.80 is not enormous between the two formulations; especially if for the Primasil formulation, processing and mixing have to be done more than once. Money is then lost by using the machinery and operators for a second times as maybe the need of advice from QA, R&D or lab persons. If the delivery of the compound or product does not arrive on the time given to the customer, refund may be asked to Primasil or lost of the market can happen.

Future work

The last route possible to make silicone sponges is the use of platinum cure. Dow Corning is utilising this cure system for their sponge products. In their literature, Dow's scientists say that the platinum cure improves the whiteness and the compression set recovery of the sponge. Rhodia's platinum curing system was used instead of peroxides in BIH formulation. Several trials were carried out in the oven (method 1, part 9-3-1) and with the extruder (method 2, part 9-3-2). Formulations are given in table 70. The sponge compound cured and blew in the oven so the mix was then extruded. The sponge obtained was whiter than the BIH sponge with peroxides cure and its skin was thicker but the sizes of the cells were too big. The density achieved was 0.50 g/cm3. From there, some work was done by using the Rheometer in order to increase the curing time to allow the formation of more cells by varying the amount of the platinum components (C.f. appendix 13 for the Rheometer curves). It was very difficult to vary the amount of platinum components because of the presence of three components and because Rhodia is keeping secret the functioning of the platinum cure; the understanding of its reaction is not well known. In order to get a higher cell density, more work is needed on the rate of platinum cure to keep all gases trapped in the silicone rubber as well on the conditions of extrusion and curing with HAV.

	Mix 1		Mix 2		Mix 3		Mix 4	
Materials	pph	g	pph	g	pph	g	pph	g
MF40U	80	739.17	80	739.17	80	739.17	80	739.17
MF240U	20	184.79	20	184.79	20	184.79	20	184.79
MPA1	0.50	4.62	2	18.48	2	18.48	1	9.24
PA2000	2	18.48	2	18.48	3	27.72	2.47	22.82
H68	1.23	11.36	0.50	4.62	0.5	4.62	1.23	11.36
BIH	4	36.96	4	36.96	4	36.96	4	36.96
Water	0.50	4.62	0.50	4.62	0.50	4.62	0.50	4.62

Table 70: BIH formulations with platinum curing system

To conclude, Primasil should work in collaboration with Rhodia to understand and to improve the use of platinum cure in BIH formulation and for the extrusion condition of platinum compound. It also may be useful to utilise Dow Corning's bases and platinum cure in BIH formulation and to compare the results obtained from both suppliers' products.

REFERENCES

) Walter Noll, Chemistry and Technology of Silicones, 1968.

) An introduction to the chemistry of silicones, 2nd edition, New York, John Wiley and Sons, 1951

) C. Friedel and A. Ladenburg, Liebigs Ann. Chem 159, 259 (1871)

) G.G. Freeman, Silicones, an introduction to their chemistry and applications, 1962

) Friedel C. and Crafts, J.M., C.R. Acad. Sci., Paris, 1863, 56, 592

) M.J.Hunter, J. Amer. Chem. Soc. 71, 2918 [1949]

) .R. Dvornic and R.W. Lenz, High Temperature Siloxane Elastomers, 1990.

) S.Al-Malaika (ed.), "Reactive Modifiers for Polymers), Blackie Academic and Professional, hapman and Hall, London (1997), chapter 2

) J.F. Hyde and R.C. Delong, J. Am. Chem. Soc., 63, 1194, 1941.

0) M.J. Hunter, E.L. Warrick, J.F. Hyde and C.C. Currie, J. Am. Chem. Soc., 68, 2284, 1946

1) Gutoff, Industr. Engng Chem., 1957, 49, 1807

2) Nostrard Reinhold, Handbook of Silicone Rubber, 1978

3) J.R.Harper, A.D.Chipman and G.M. Konkle, Rubber Wld. 137, 711 [1958]

4) Polymer Processing, D.H Morton-Jones, published by Chapman and Hall, 1989, ch. 3-4-8-9-11

5) S-T Lee, Foam Extrusion, Principles and Practice, 2000

) Plastics Compounding Redbook, Advanstar Communications, pp.18-20, 1998, Cleveland, OH

7) Thomas H. Ferrigno, Rigid Plastics Foams, second edition, 1967.

) Urethane Technical Bulletin V-3 and VF-4, The Dow Chemical Co.

9) Modern Plastics, 39, 82, 1961.

0) Fielding, H.C. and Pollock, J.M (to Imperial Chemical Industries Ltd) British Patent 968, 109, ugust 26, 1964.

) Goldfein, S. and Calderon, J., J. Applied Polymer Sci., 9, 2985, September 1965.

2) Bailin, R.C., SPE Regional Technical Conference, Plastics Foams, Buffalo, New York, October 1961.

) Dow Chemical Co., Plastics Dept., Bulletins 171-90, 171-120, and 171-169.

) Lambert, F., Mod. Plastics, 39, 109, (1961); 39, 113 (1961).

) Rauwendaal, C., Screw Design For Foam Processing, Plastics World, 38, May 1997.

) Han, C. Dard Ma, C. Y, J. Applied Polymer Sci., 28, 831 (1979).

7) White, J., Twin-Screw Extrusion, Chapter 7 and 10, Hanser, New York, 1991

) Thiele, W.C. 2000 "Foam Extrusion Machinery Features", in Principles of Thermoplastic Foam xtrusion. S-T. Lee, ed. Lancaster, PA: Techromic Publishing Co. Inc.

) RAPRA, Guide to Rubber and Plastics, Test equipment, second edition, 1979.

) R. P. Brown, Physical Testing of Rubbers, 1979.

) ISO 667, Determination of rate of cure using the shearing Disc Viscometer, 1975

2) John M. Dealy, Rheometers for Molten Plastics, a practical guide to testing and property
easurement, 1982.

3) BS 903 part 2: 1995, Tensile Strength and Elongation

4) ISO 314 979, Tear Strength, First edition 1979.

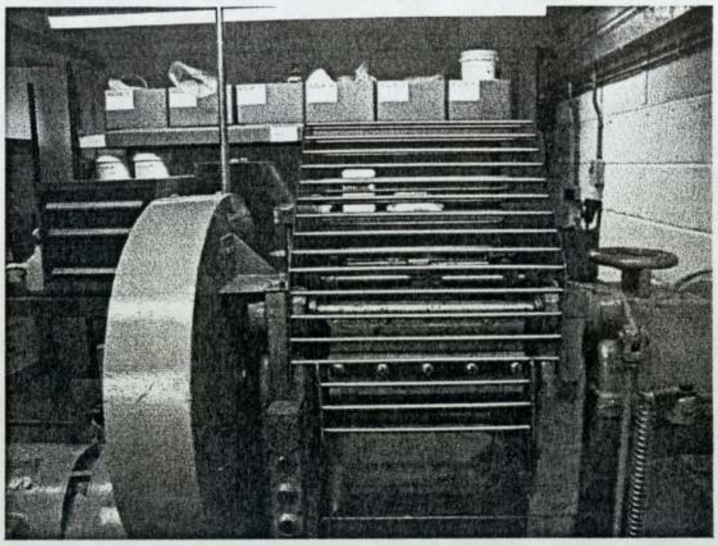
5) ISO 2781, Vulcanised Rubbers, Determination of density, 1975

6) BS 903 part A1: 1996, Determination of density

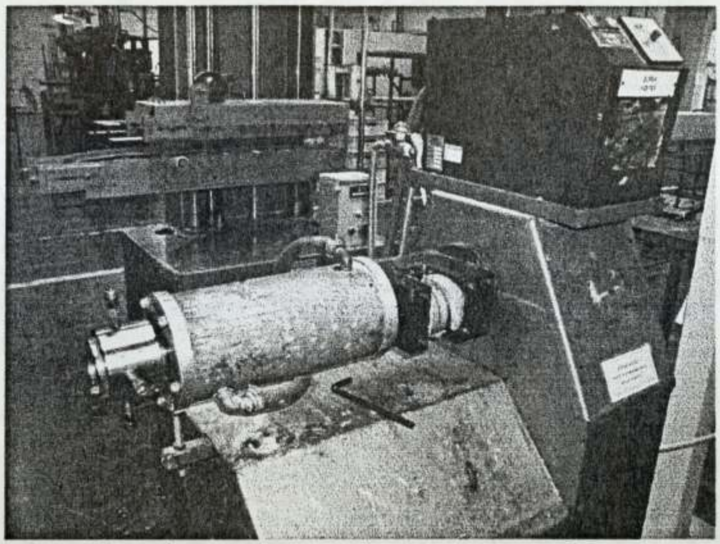
7) ASTM D395-89, method B test piece 2, Compression Set, Volume 09.01.1990

Appendix 1: Two-roll Mill used to compound silicone rubber with different ingredients (Primasil: laboratory equipment

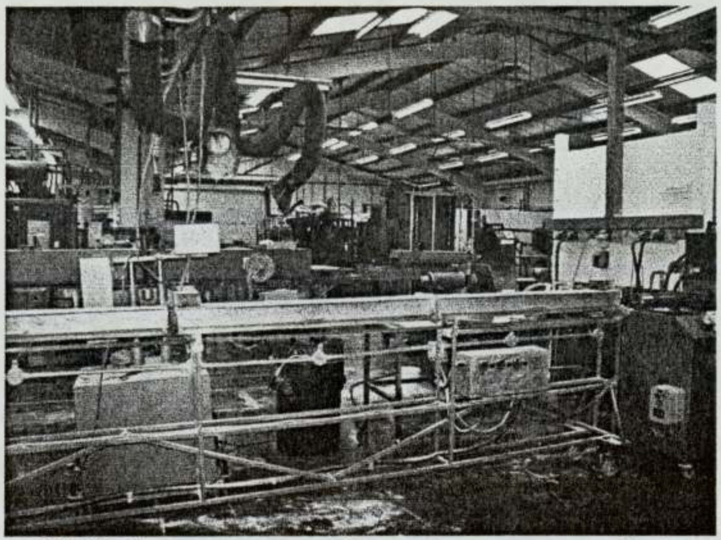
This two-roll mill (2 kg, Mattew Johnson & Co Ltd) was used to prepare the sponge compound (lab scale).



Appendix 2: Extruder used to produce silicone foams (Primasil: production equipment)

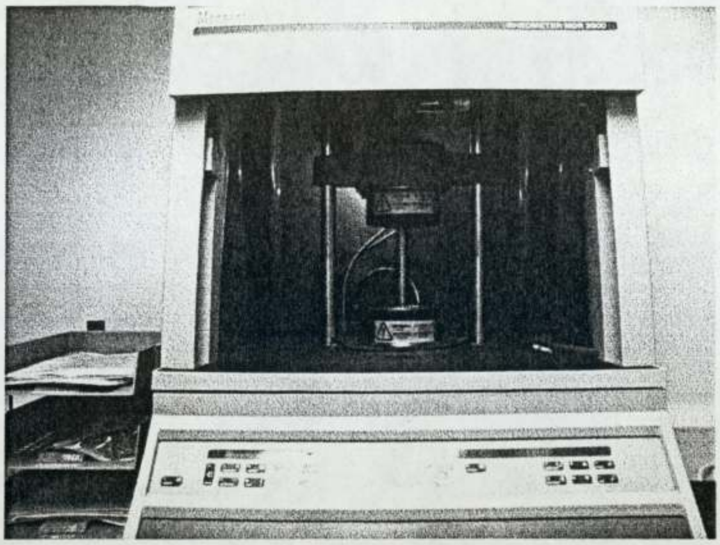


Extruder used to produce sponge products



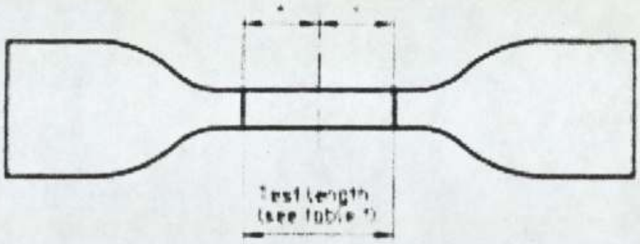
HAV: three meters, used to make sponge products

Appendix 3: Rheometer equipment (Primasil: laboratory equipment)

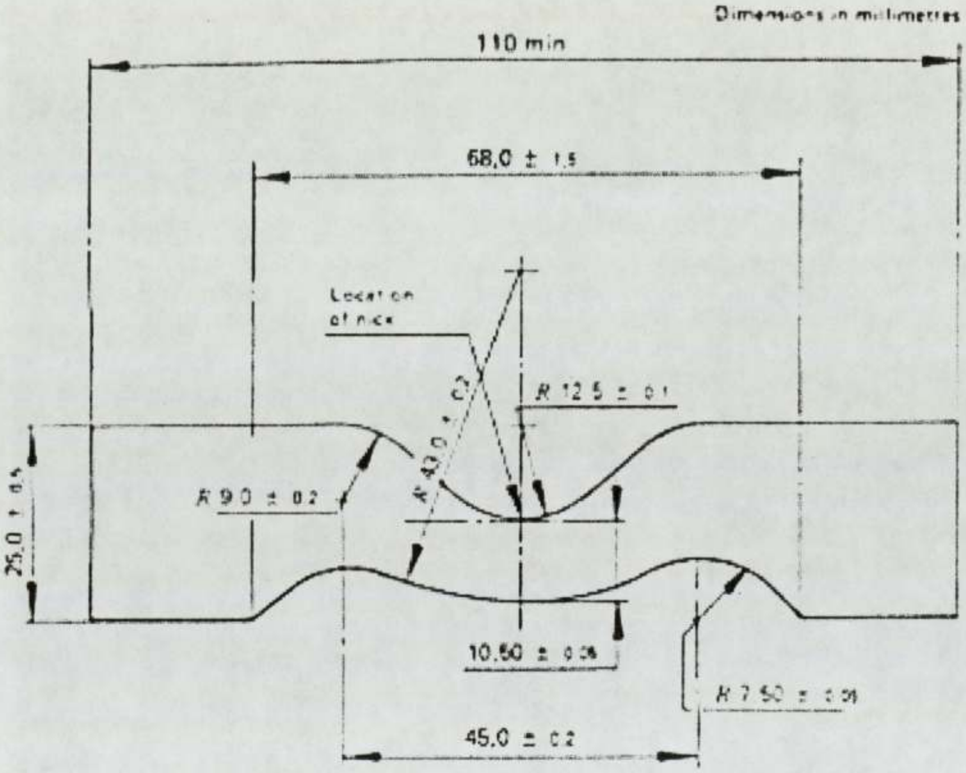


It is used to control the quality of cure of silicone compounds.

Appendix 4: The shape of Dumbell and tear samples used for the mechanical tests



Dumbbell specimen

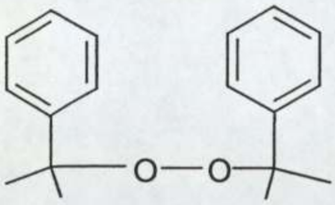


Tear specimen

Appendix 5: List of material used for the experiments

1- Peroxides:

Di-cup: Dicumyl peroxide



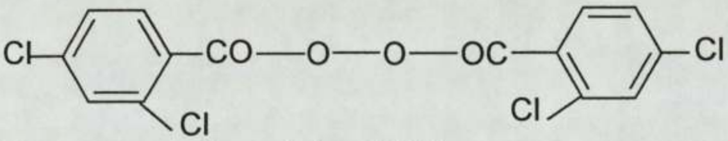
Colour: white

Density: 1.02 g/cm3

Form: semi-crystalline solid

Range of temperatures to use Di-cup:115 to 140˚C

PDS: bis (2, 4-dichlorobenzoyl) peroxide, paste, 50 % in silicone oil

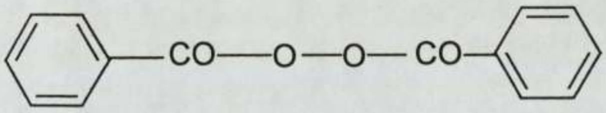


Temperatures of use: 100 to 120˚C

Appearance: white paste

Density: 1.18 g/cm3

Lucidol: dibenzoyl peroxide



Temperature of use:160 to 170˚C

Molecular weight: 242.2

Appearance: white paste

Density: 1.12 g/cm3

Varox

Platinum cure: MPA1, H68, PA2000 (catalyst)

2- Pigments

MB01: mix 50 pph of gum 901 and 50 pph of TR28

Colour: white

Appearance: rubber crepe

MB 76: mix 50 pph of gum 901 and 50 pph of black pigment

Colour: black

Appearance: rubber crepe

MB77: mix 50 pph of gum 901 and 50 pph of white and black pigment

Colour: grey

Appearance: rubber crepe

3- Bases from Rhodia

MF40U: Silicone master-batch compound of polyorganosiloxane and amorphous silica

Use for regular cell structure and good surface finish.

Form: pasty solid, translucent

Decomposition temperature >200 C

SG: 1.09 g/cm3

MF240U: silicone master-batch

Give low compression set

MF25U: Product based on polyorganosiloxanes and silica

Form: Pasty solid, beige

Decomposition temperature > 200C

SG: 1.14 g/cm3

Gum 901: polydimethylmethylvinylsiloxane, dimethylsiloxane, methylvinyl terminated gum

Appearance: Solid paste

Colourless

No odour

SG: 0.97 g/cm3

4- Bases from Wacker

R401/40: polydimethylsiloxane with vinyl groups and fillers

R401/30: polydimethylsiloxane with vinyl groups and fillers

R401/20: polydimethylsiloxane with vinyl groups and fillers

Appearance: Paste, opaque

Density: 1.12 g/cm3

5- Other ingredients

Min-u-sil

Bex: carrier and sodium bicarbonate mixture

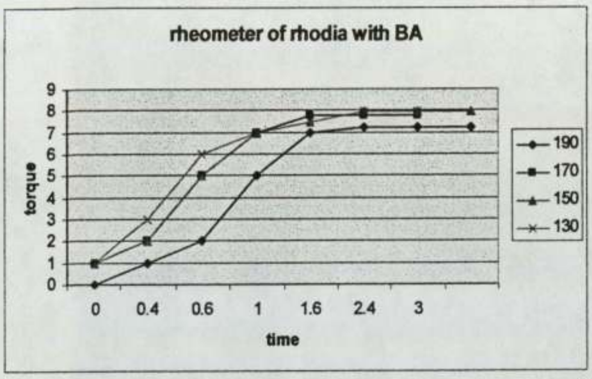
F-celite or Superfloss: flux calcined diatomaceous earth for filler and speciality application

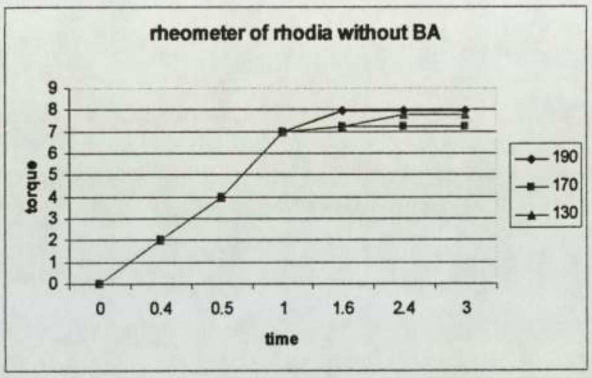
Colour: white

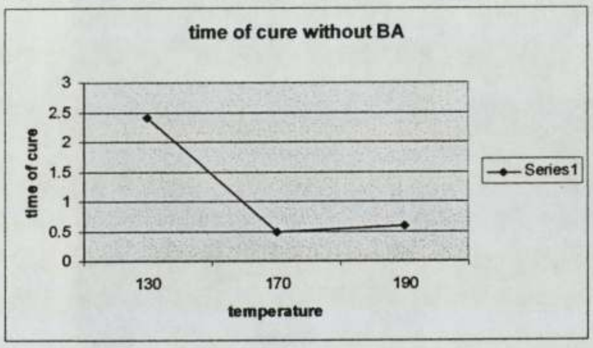
Appearance: powder

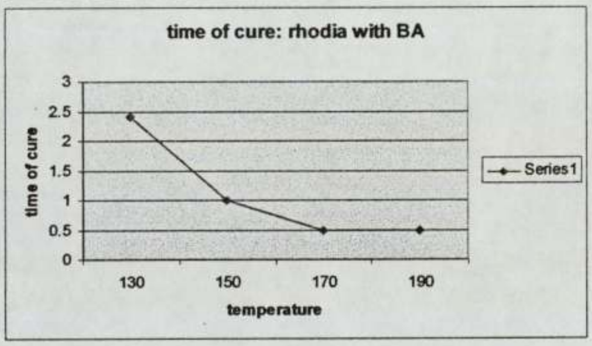
Appendix 6: Graphs showing the effect of Rhodia blowing agent

Experiments were carried out on the time and cure of the Rhodia formulation to investigate whether the blowing agent had any influence on these two parameters. The experiment did not show any differences between the Rheometer curves for the normal formulation (table 47) and for the formulation without any blowing agent. It is difficult to distinct two steps of process: one to cure the compound and the other one to blow the compound which may suggest that both steps take place at the same time or also that under pressure the compound did not have the time to blow properly.


rheometer of rhodia with BA


rheometer of rhodia without BA


time of cure without BA


time of cure: rhodia with BA

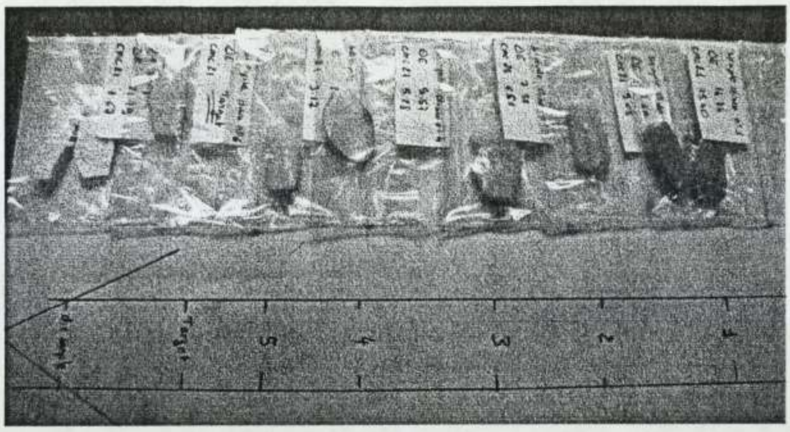
Appendix 7: Formulations and results for the discolouration in Rhodia formulation

The problem was discolouration on Rhodia sponge extruded parts after post-cure. An experiment in the oven as *method 1* was done to understand better the problem and to resolve it. Six mixes were prepared as method 9-1 and tested under identical conditions. The samples were cured for 20 minutes at 200 °C and post-cured for 4 hours at 200 °C. The six mixes were all different. The aim was to find why there was a discolouration by eliminating each ingredient in turn.

Discolouration of RHODIA formulation

	MF40U	MF240U	Lucidol	PDS	PLO	Bex	R401/30	After cure: oven 20 mins@200°C	After post-cure: 2hrs@200°C
1	95 pph	5 pph	1.27 pph	0.42 pph				no discolouration	discolouration
2	95 pph	5 pph		1.5 pph	1 pph			no discolouration	no discolouration
3	95 pph	5 pph	1.27 pph	0.42 pph		1 pph		important discolouration	Darker
4	95 pph	5 pph	1.5 pph		1 pph			nothing	small discolouration in the middle
5			1.27 pph	0.42 pph	1 pph		100 pph	discolouration	same discolouration

Appendix 8: Scale of discolouration

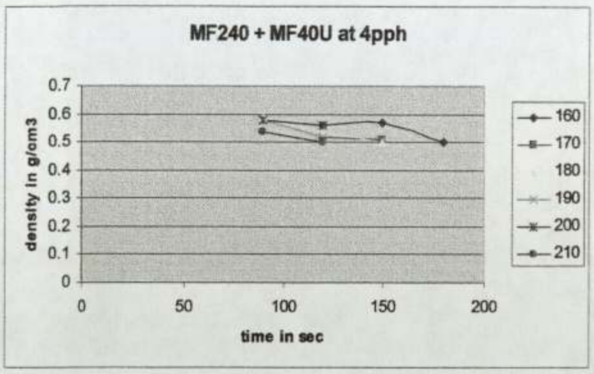


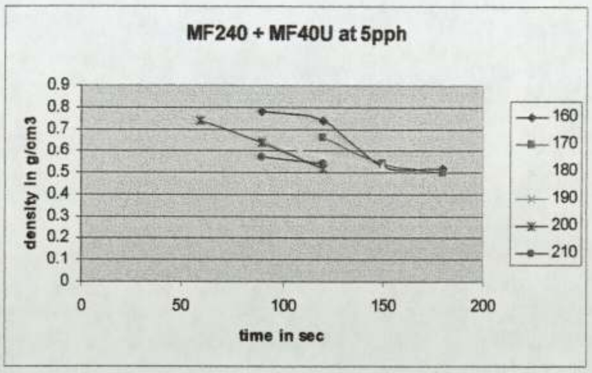
Light colour (white) ⟷ Dark colour (dark brown)

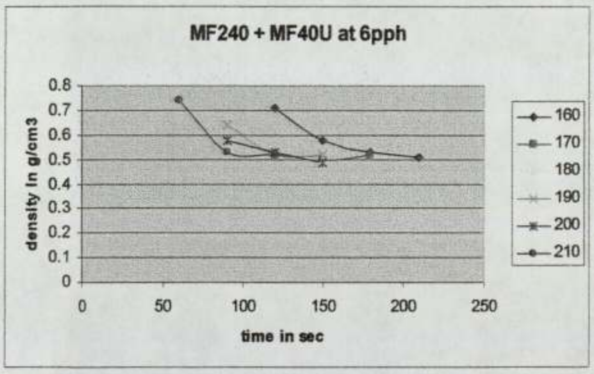
This scale is used to grade the discolouration of silicone foams obtained with Rhodia formulation.

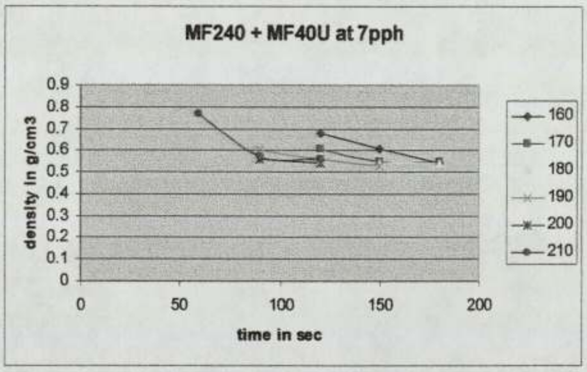
Appendix 9: Graph showing density obtained for different amounts of BIH

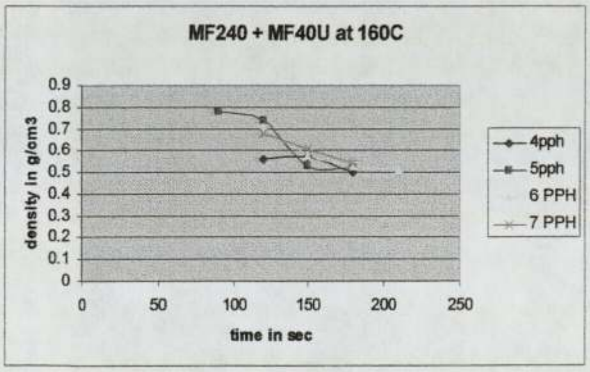
The aim of this experience was to see if by increasing or decreasing the amount of BIH, the density of the sponge change. The aim was to obtain a density lower than 0.5 g/cm^3. The amount of BIH was increased until 7 ppH but the density did not go lower than 0.5 g/cm3. The temperature and the time of curing of the sample were also varied.

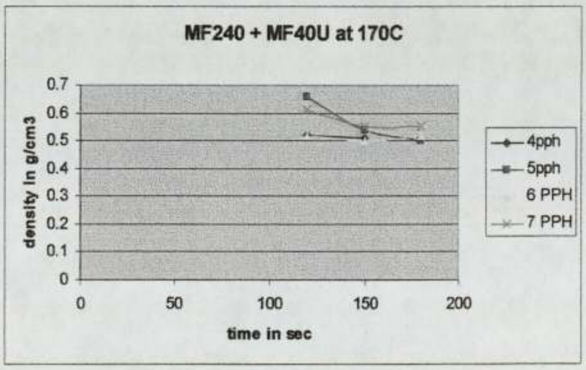


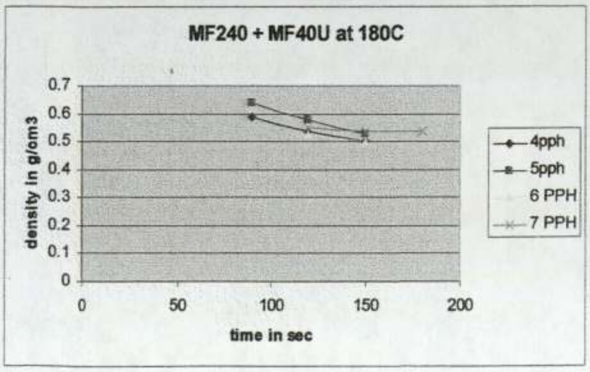


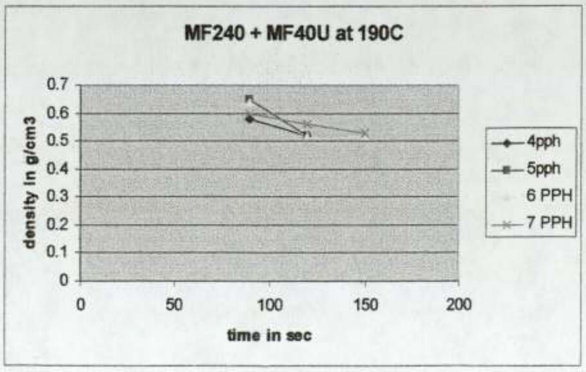


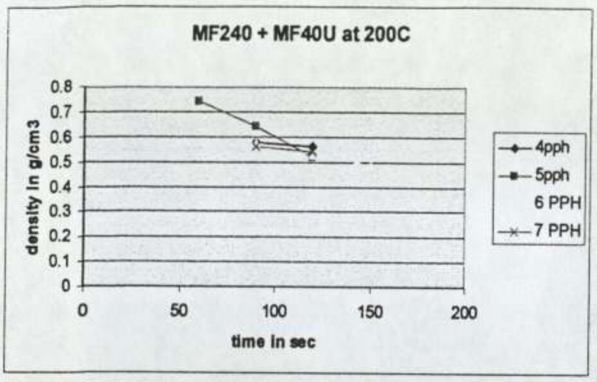


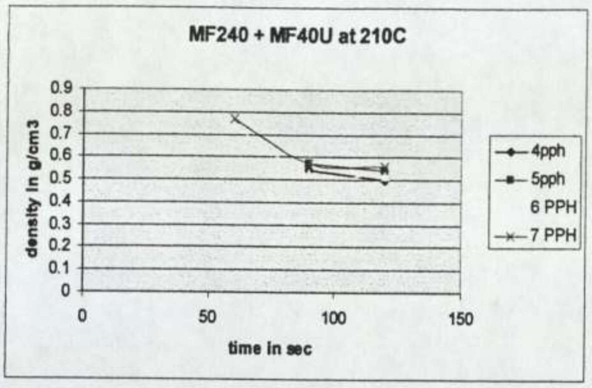


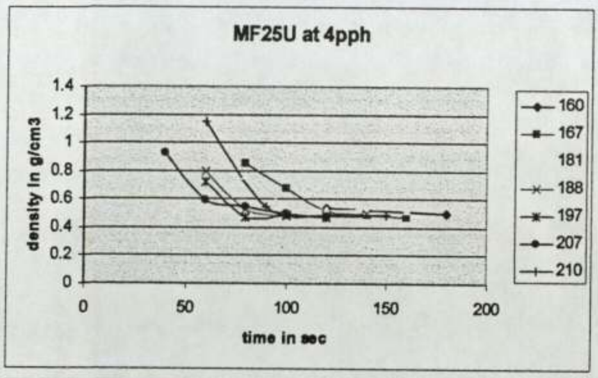


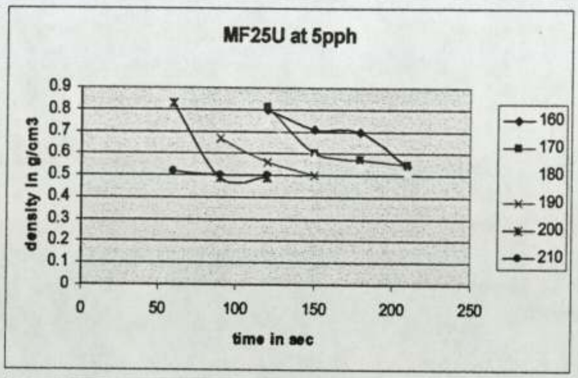


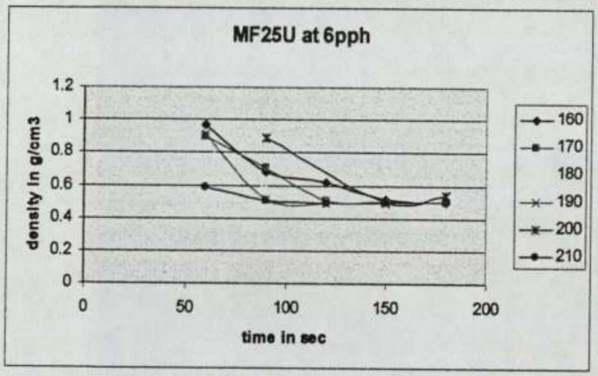


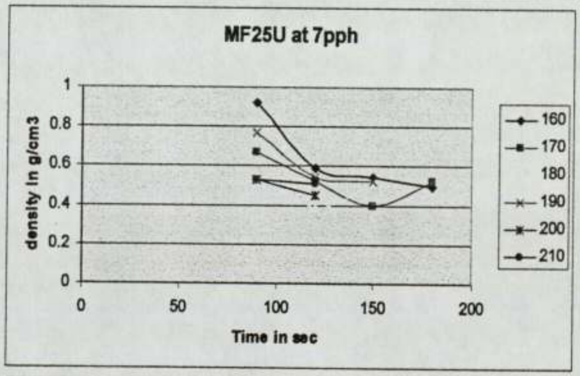

MF240 + MF40U at 200C

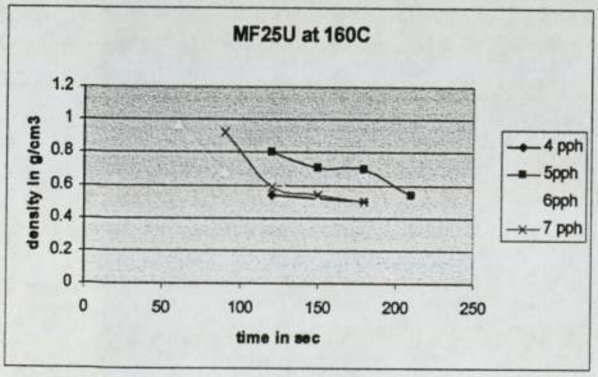

MF240 + MF40U at 210C

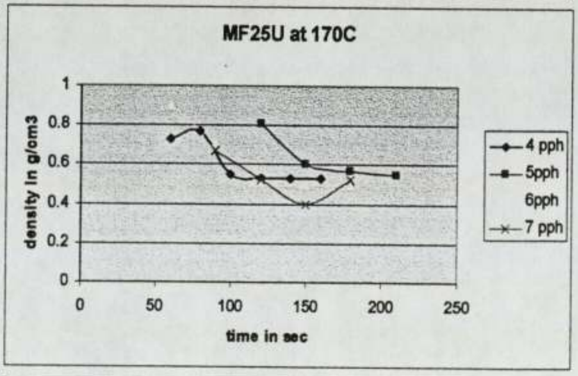

MF25U at 4pph

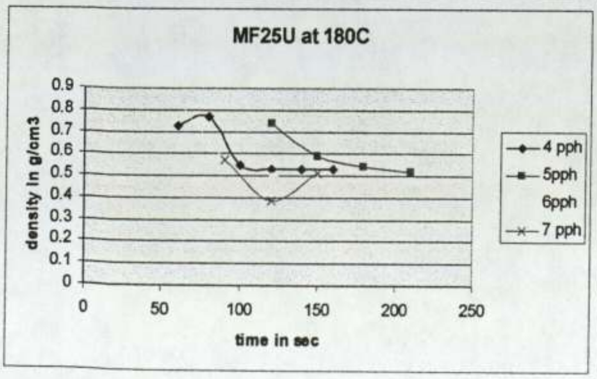

MF25U at 5pph

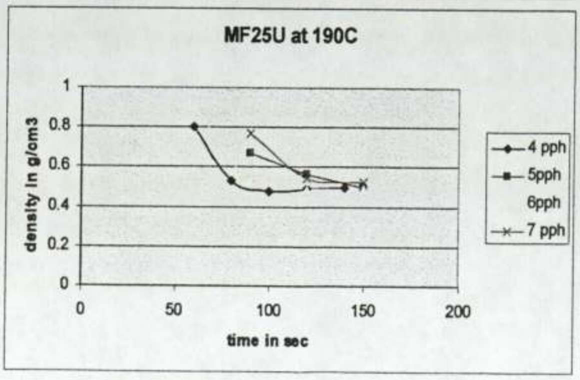

MF25U at 6pph

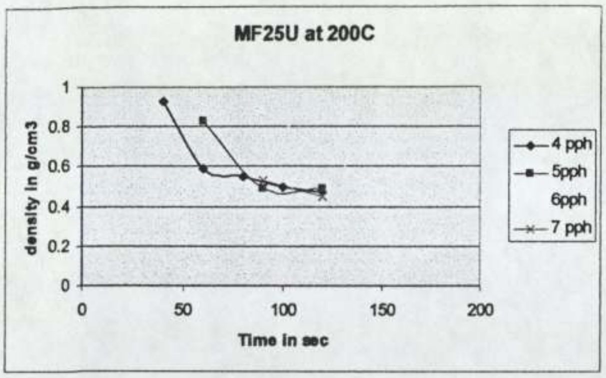

MF25U at 7pph

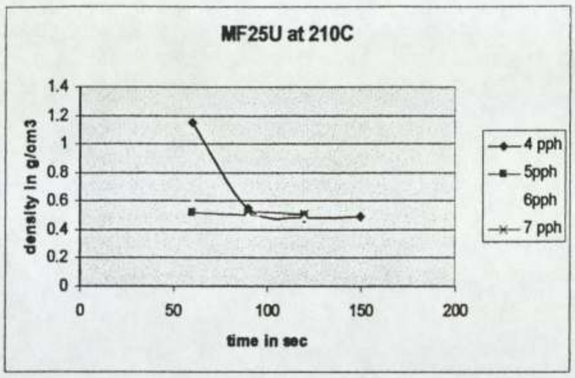

MF25U at 160C


MF25U at 170C


MF25U at 180C


MF25U at 190C


MF25U at 200C
density in g/cm3
1
0.8
0.6
0.4
0.2
0
0
50
100
150
200
Time in sec
4 pph
5pph
6pph
7 pph


MF25U at 210C
density in g/cm3
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
50
100
150
200
time in sec
4 pph
5pph
6pph
7 pph

Appendix 10: Design experiment

Design Experiment:

Std	run	Block	Lucidol pph	PDS pph	BIH pph	Time min	Temperature C	density g/cm3
1	2	Block 1	0.70	0.42	3.00	2.00	220.00	0.43
2	3	Block 1	0.70	0.42	3.00	2.00	220.00	0.43
3	4	Block 1	1.40	0.42	3.00	2.00	120.00	0.54
4	5	Block 1	1.40	0.42	3.00	2.00	120.00	0.66
5	6	Block 1	0.70	2.00	3.00	2.00	120.00	0.84
6	7	Block 1	0.70	2.00	3.00	2.00	120.00	0.85
7	8	Block 1	1.40	2.00	3.00	2.00	220.00	0.58
~~8~~	~~9~~	~~Block 1~~	~~1.40~~	~~2.00~~	~~3.00~~	~~2.00~~	~~220.00~~	~~0.00~~
9	10	Block 1	0.70	0.42	10.00	2.00	120.00	0.49
10	11	Block 1	0.70	0.42	10.00	2.00	120.00	0.54
11	12	Block 1	1.40	0.42	10.00	2.00	220.00	0.48
12	13	Block 1	1.40	0.42	10.00	2.00	220.00	0.47
13	14	Block 1	0.70	2.00	10.00	2.00	220.00	0.39
14	15	Block 1	0.70	2.00	10.00	2.00	220.00	0.40
15	16	Block 1	1.40	2.00	10.00	2.00	120.00	0.43
16	17	Block 1	1.40	2.00	10.00	2.00	120.00	0.44
17	18	Block 1	0.70	0.42	3.00	12.00	120.00	0.74
18	19	Block 1	0.70	0.42	3.00	12.00	120.00	0.66
19	20	Block 1	1.40	0.42	3.00	12.00	220.00	0.46
20	21	Block 1	1.40	0.42	3.00	12.00	220.00	0.51
21	22	Block 1	0.70	2.00	3.00	12.00	220.00	0.53
22	23	Block 1	0.70	2.00	3.00	12.00	220.00	0.47
23	24	Block 1	1.40	2.00	3.00	12.00	120.00	0.77
24	25	Block 1	1.40	2.00	3.00	12.00	120.00	0.58
25	26	Block 1	0.70	0.42	10.00	12.00	220.00	0.43
26	27	Block 1	0.70	0.42	10.00	12.00	220.00	0.44
27	28	Block 1	1.40	0.42	10.00	12.00	120.00	0.41
28	29	Block 1	1.40	0.42	10.00	12.00	120.00	0.47
29	30	Block 1	0.70	2.00	10.00	12.00	120.00	0.49
30	31	Block 1	0.70	2.00	10.00	12.00	120.00	0.58
31	32	Block 1	1.40	2.00	10.00	12.00	220.00	0.35
32	33	Block 1	1.40	2.00	10.00	12.00	220.00	0.40
33	1	Block 1	1.05	1.21	6.50	7.00	170.00	0.38

Designed experiment analysis

The design has been analysed to give the most accurate model, while not introducing errors associated with including Factors for hierarchical consistency.

Starting at the Design Page, I have sorted the runs into Standard order so that I can see where there may be problems with the data. Immediately you can see that one of the experiments has not worked and that you have ignored this data (this will show up in the analysis later on).

Otherwise the data looks fine.

The Analysis:

The first time that I analysed the results, it suggested that a transformation of the data was necessary; it has therefore been transformed to an inverse square root (TRANSFORM PAGE).

In the EFFECTS PAGE, you can see that I have selected the factors, A, B, C and E, plus their interactions of AE, BC and CE.

Term D (Time) has no statistical effect on the Density of the Sponge and so is not selected.

In the ANOVA PAGE, you can see that the B term is not significant (PROB>F is greater than 0.1) it is uncertain to how large an effect the A term has (PROB>F is larger than 0.05, but less than 0.1), but these two terms must be included to give hierarchical consistency (they are involved in INTERACTIONS).

The interaction terms (AE, BC and CE) are all significant as are terms C and E.

The Curvature of the model also appears to be significant; this means that the centre point experiment of the design is statistically important to the model.

The R-Squared and Adjusted R-Squared values are in good agreement and close to a value of 1.0; this means that the model is a good estimation of the system.

The DIAGNOSTICS PAGE

The Normal Plot of Residuals shows that the residuals are nearly linear, this suggests that the data is Normally Distributed and therefore can be used as a statistical model.

The Residuals V's Predicted shows a random pattern, this means that the model does not contain errors that affect one part of the design more than another; this is supported in the Predicted V's Actual graph too.

Residuals V's Run shows a random pattern, which indicates that there is no outside influence of the results from time/machinery factors.

Residuals V's Factors shows no real suggestion of large errors caused by the different levels of Factors.

Outlier T and Cooks Distance both show no large errors in the results.

Leverage shows two results that have different leverage to the other experiments, the centre point for the Design, and Std Run 7. They have larger leverage because they have only one replication, the centre point because the experiment was only done once, and Std Run 7 because the replication has been omitted (the result has been ignored in the design because the Density could not be measured). This means that these two points will have more effect on the model than others.

Box Cox shows that the data needed to have a transformation of Inverse Square root, this has been selected.

MODEL GRAPHS.

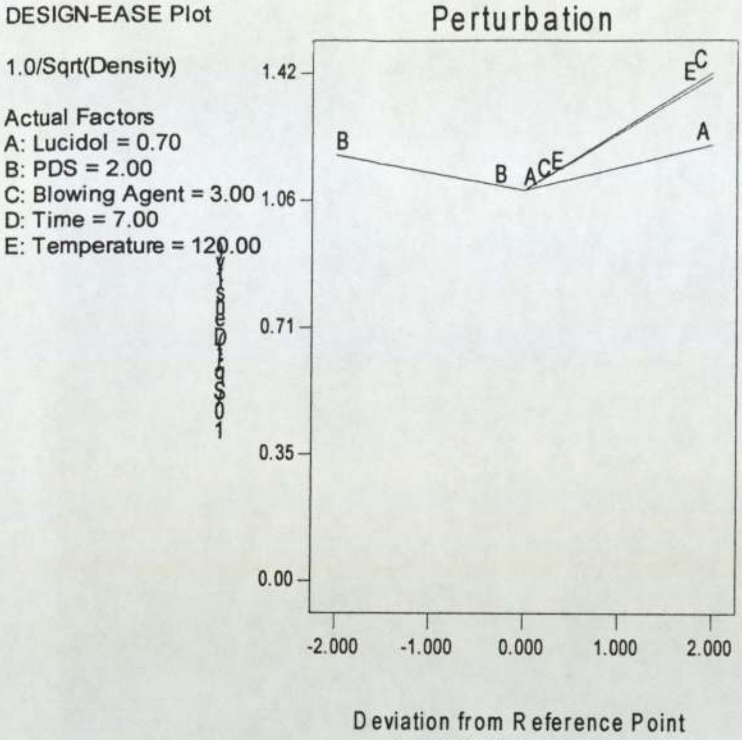
Firstly look at the One Factor plots for each of the Terms A, B, C, and E.
You can see that at the top of each graph for A, B, C and E you get a warning that they are involved in Interactions, so the most useful Terms to look at are the Interaction terms AE, BC and CE.

These graphs show the effect of the interaction between each factor and its effect on 1/density^0.5. You can see that the Interaction of CE has the largest effect (the gradient of the lines is greatest).

You can also see that some of the Interactions (AE for example), show that when one Term (E) is at it's lowest value, an increase in the other Term (A) results in a positive gradient (1/density^0.5 increases, Density of Sponge decreases), but when Term E is its highest value, an increase in A results in a negative gradient (1/density^0.5 decreases, Density of Sponge increases). You can see that this also occurs for Interaction BC, but not for CE. It can give you valuable information about how your factors are affecting each other.

Looking back at the terms A, B, C and E, you can see that the graphs with the greatest gradients are C and E. These are the factors which have the biggest effect on the 1/density^0.5 of the sponge.

I then looked at the Perturbation Plot and selected experimental conditions to give the highest and lowest Density of Sponge from the Model. (See Screenshot showing Highest Density conditions).



You can see that Term A (Lucidol pph), C (Blowing Agent pph) and E (Temperature) are all at the lowest values they can be in this Model.
Term B (PDS pph) is at the highest value.

You can change the Perturbation Plot to show the experimental condition that will give the lowest Density of Sponge if you want to!

RESULTS:

The following are Experimental Conditions that will give the Highest and Lowest Density Sponges;

Highest:

Lucidol = 0.7 pph
PDS = 2.0 pph
Blowing Agent = 3 pph
Time = Between 2 and 12 minutes (this is unimportant to the Model)
Temperature = 120 Deg C

The Sponge produced would be expected to have a density of ~ 0.84 g/cm^-3

Lowest:

Lucidol = 0.7 pph
PDS = 2.0 pph
Blowing Agent = 10 pph
Time = Between 2 and 12 minutes (this is unimportant to the Model)
Temperature = 220 Deg C

The Sponge produced would be expected to have a density of ~ 0.39 g/cm^-3

FURTHER WORK

Looking at the results and the information gained from ANOVA, it is clear that the greatest effect on Density is caused by Blowing Agent and Temperature, then by the Interactions of Lucidol and Temperature, PDS with the Blowing Agent and the Blowing Agent with Temperature.

The 3D Graph of the model also indicates that outside of the Design Space, it may be possible to have even Higher of Lower Density Sponges.

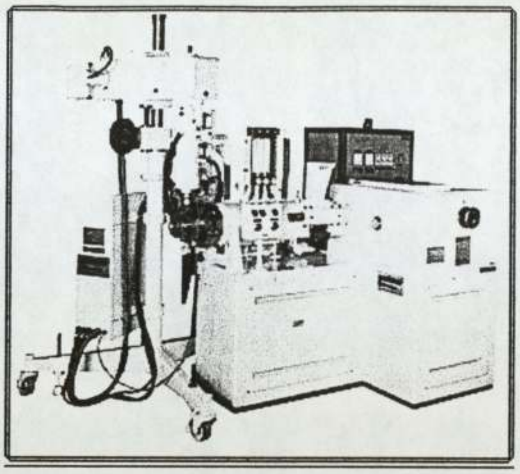
Therefore;

If you want to have a Higher Density Sponge than those suggested above, maybe you should look at doing another Design where the values for Blowing Agent is in the range of 1.0-3.0 pph and Temperature is 90-120 Deg C? (I seem to remember you telling me that your catalyst requires a certain temperature to initiate, but I can't remember what temperature that is!!).

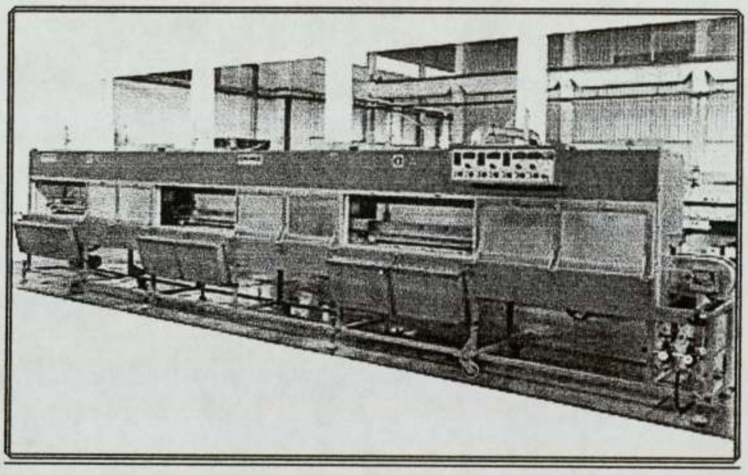
If you want to have a lower Density Sponge, then maybe try a Design where the values for Blowing Agent is 10-15 pph and Temperature is 220-250 Deg C?

Richard

Appendix 11: Picture of Colmec equipment (Italy)



Extruder from Colmec



HAV from Colmec

Appendix 12: Condition of extrusion in Colmec

Appendix 12: Condition of extrusion in Colmec

COLMEC SPA

COLMEC LAB

MD 1240
REV. 0
DATA

CUSTOMER: PRIMASIL **DATA:** 17/11/2003 -----------
COMPOUND: SILICON SPONGE WHITE
EXTRUDER: TGS90 **SCREW:** 12D
MACHINES: PRE VULCANIZER OVEN Type PVO/9/600 HOT AIR OVEN Type FAC/V12.3

Test	TGS90	Pre-vulcanizer	FAC/V12.3						Oven belt speed (m/min.)	Results
N°	Rpm	Temp. °C	Fan r.p.m.			Temperature °C				
			Zone 1	Zone 2	Zone 3	Zone 1	Zone 2	Zone 3		
1D	6,2	---------	2000 3000	2000 3000	2000 3000	150	180	210	4,0 (5,3)	CURED
2D	12,2	---------	700 ------	1100 -------	2000 1000	160	180	210	2,3 (3,3)	CURED
1E	4,5	---------	700 ------	1100 ------	2000 1000	160	180	210	2,3 (2,6,)	CURED
2E	4,5	---------	600 ------	600 -------	9000 1300	135	160	180	1,8 (2,3)	CURED
F	4,5	-----------	600 ------	600 -------	9000 1300	135	160	180	1,8 (2,3)	CURED

NOTE: PROFILE D , E F NO STRAINER

D-> sponge strip
E -> sponge cord
F -> sponge tube

Appendix 13: Rheometer curves of platinum compounds

This part was done to work on lowering the time of cure in order to leave time for the foaming to take place. It was very difficult to control the platinum cure because there are three compounds used in Rhodia platinum cure so three variables. More work is needed.

RIMASIL LTD **TEST RESULTS** **21/01/04 Page: 1**

ompound PLATINUM Description:

eparation method: - None -
geing method: - None -

derno.: Batchno.: MIX A Testno.: 2

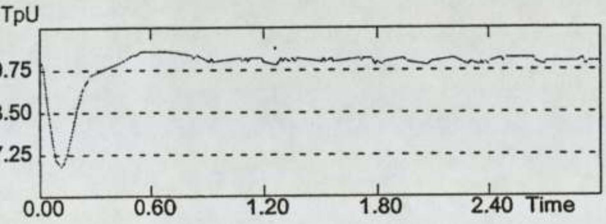
---

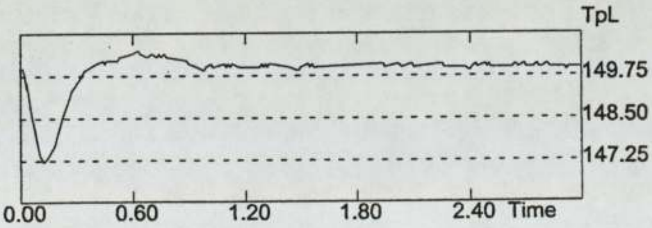
stcode: 30000 Descr.: Standard Rheometer Test ISO 3417

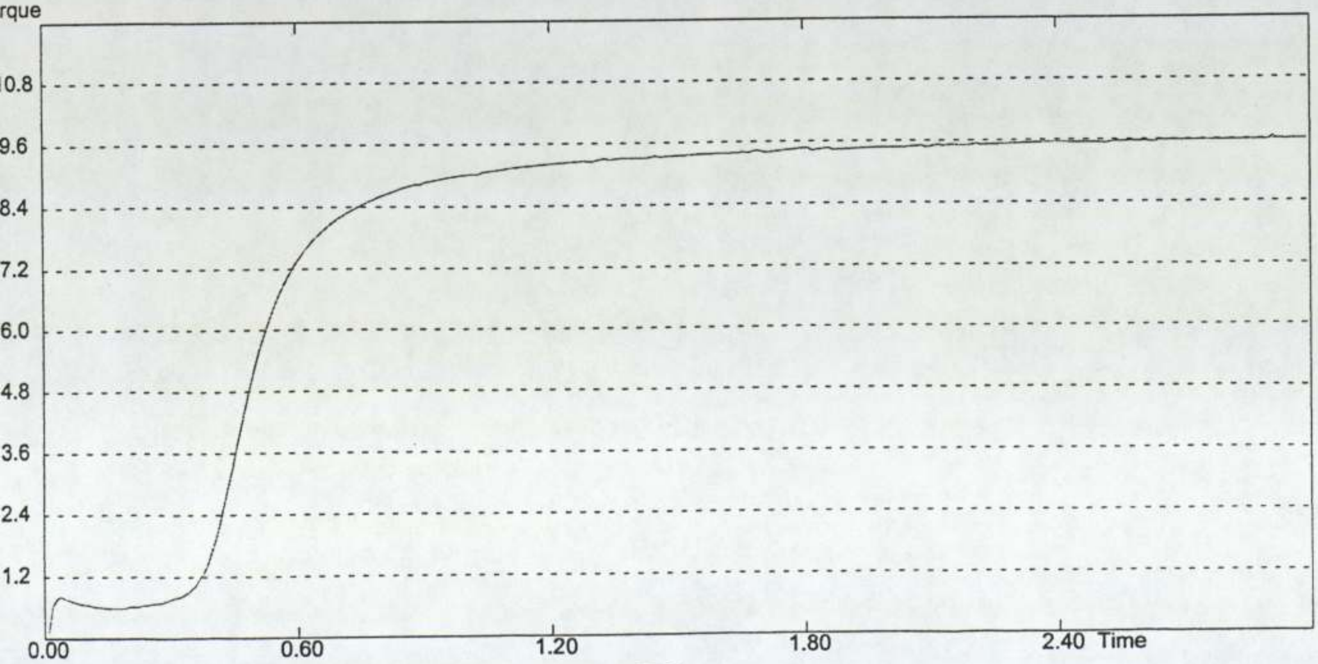
riable		Value	Unit	LSL	USL
st temp		150.0	degrees		
st time		3:00	min/sec		
		0.60	dNm		
H		9.65	dNm		
		0:26	min/sec		
		0:30	min/sec		
		0:50	min/sec		

Testdate	21/01/04 10:14 MW
Validated by	
Limit version	0
Limits	Not found
Limits remark 1	
Limits remark 2	
Remark 1	
Remark 2	
Production date	21/01/04
Hardness BPC	
Hardness APC	
S.G.	
Tensile	
Elongation	
Tear	
Comp Set	
Delta E	
CMC 2:1	
Plasticity	
Last changed	21/01/04 MW

Status: **Tested**







PRIMASIL LTD **TEST RESULTS** **21/01/04 Page: 1**

Compound PLATINUM Description:

Preparation method: - None -
Ageing method: - None -

Orderno.: Batchno.: MIX B Testno.: 2

---

estcode: 30000 Descr.: Standard Rheometer Test ISO 3417

ariable		Value	Unit	LSL	USL
est temp		150.0	degrees		
est time		3:00	min/sec		
L		0.22	dNm		
H		5.67	dNm		
2		0:48	min/sec		
0		0:51	min/sec		
0		1:29	min/sec		

Testdate	21/01/04 10:09 MW
Validated by	
Limit version	0
Limits	Not found
Limits remark 1	
Limits remark 2	
Remark 1	
Remark 2	
Production date	21/01/04
Hardness BPC	
Hardness APC	
S.G.	
Tensile	
Elongation	
Tear	
Comp Set	
Delta E	
CMC 2:1	
Plasticity	
Last changed	21/01/04 MW

Status: **Tested**