STUDIES IN THE CONTROL OF PROPERTIES OF

POLYURETHANE FOAMS

THESIS

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A B S T R A C T

There are a lot of local polyurethane foam manufacturers in Nigeria who appear not to have properly correlated the effect of the various foam ingredients on foam properties. The effect of some of the variables in polyurethane foam preparation on foam properties have been investigated, Excess Tolylene di-isocyanate (TDI) in flexible polyurethane foam formulation has no significant effect on physical properties but trace amounts of water in the form of moisture can affect foam properties significantly. Trace amounts of sodium hydroxide solution and sodium bicarbonate in flexible foam formulations respectively catalyze polyurethane foam reactions and give rise to crumbling foams. Increasing amount of freon used with a fixed amount of water gives foams of better appearance than when water is used alone. It was also observed that increase in rise height decreases foam density while tensile stress at break and initial modulus are high at low rise heights. Flexible foams have low compressive stresses before stiffening occurs and a pronounced yield point which decreases with decrease

in density. Flexible fcaras have a comparatively low hysteresis loss and hence good resilience. The density of rigid foams decrease with increase in blowing agent concentration. Rigid foams have high compressive stresses, undefined yield points and large hysteresis losses. The thermal conductivity of rigid foams (density 34-23 k g m) increased with decrease in foam density.

CHAPTER I

1. INTRODUCTION

Polyurethanes are defined as those polymers which contain the characteristic linkage $\rangle N - \underset{\underset{O}{\|}}{C} - O -$ which may be regarded as a mixed amide-ester of Carbamic acid. They have attained such commercial importance that they not only include homopolymers that fit the above definition, but copolymers both linear and crosslinked in which the urethane linkage may actually constitute a small part of the total number of linkages in the polymer chain.[1] The possible linkages are ureas, biurets, allophanates, ethers, esters, amides etc.

1.1 Development.

An attempt by Otto Bayer and his team of chemists in 1937[2,3] to circumvent the Du Pont patents on nylon 66 gave rise to the commercial development of the polyurethanes.

Of the several methods (See Fig. 1a) reported[4, 5] for the preparation of polyurethanes, the most commonly

used is not a condensation reaction but an addition reaction of isocyanate with polyol giving rise to stepwise polymerisation as shown in fig. 1b. Of the various polyurethanes made in this way, the only linear homopolymer that reached commercial importance is the polyurethane based on 1, 6 - hexanediisocyanate and 1, 4 - butanediol[1] which has some resemblance to nylon 66.

$$\left[\text{NH}\,(CH_2)_6\text{NHCO}(CH_2)_4\text{OC}\right]_n \qquad \text{----------(1)}$$

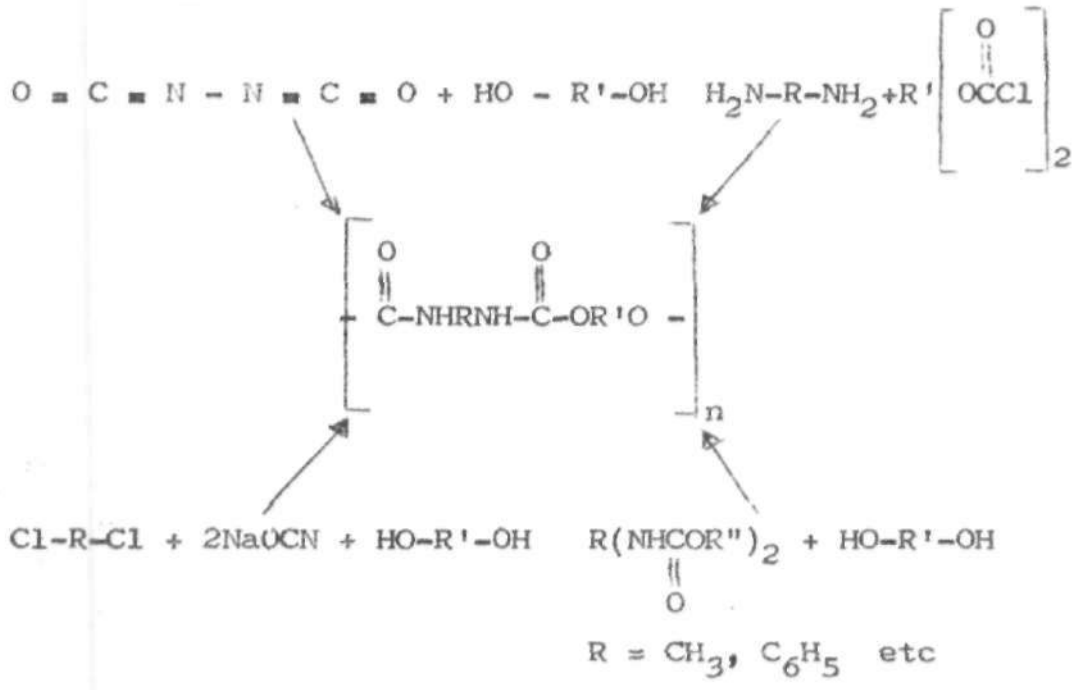


Fig. (1a)

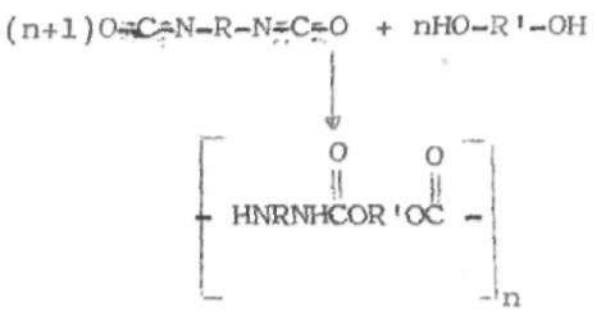


Fig. (1b)

Efforts were therefore directed to the development of copolyurethane materials such as polyurethane foams. Various polyurethanes which find applications as elastomers, fibres adhesives,[6,7] coating [8,9] etc have been prepared successfully but the most spectacular achievements occurred in the development of polyurethane foams both flexible[2,10] and rigid[11,12]. These have been accepted in a wide variety of applications since the 1940s.

1.2 Applications

The application of polyurethane foams have been predominantly in comfort cushioning, packaging, wearing apparel and in thermal insulation. Slightly cross-linked products (rigid foams) are employed in thermal insulation. Slightly cross-linked polyurethane foams (flexible foams) are mainly used in cushioning while highly cross-linked

products (rigid foams) are employed in thermal insulation purposes.

The furniture industry is a very large consumer of flexible foams for bedding, upholstery and low density rigid foams for chairshells. These traditional applications have the common factor that the foam is not seen in the finished article. The rigid foam chairshell is covered in flexible foam and this, in turn, is covered with a furnishing fabric. An inovation in this field which has already started is the use of polyurethane foams for items of furniture which can be seen, a situation made possible by the introduction of integral skin structural rigid foam and polyurethane coated fabrics. This new opening (integral skin-flexible foams) have a urethane skin of higher density than the rest of the moulding due to the reduced vapourisation (and consequently less expansion) of the blowing agent at the surface of the mould. The major application for such mouldings has been in the production of arm rests, facias, steering wheels and inserts, crash pads and bumpers in the automative industry.

As already noted in section 1.2, rigid foams are

good thermal insulators. The refrigeration industry is the largest consumer of rigid polyurethane foams. Apart from being good insulators, rigid foam has about twice the insulating value of any other commercially available insulating material,[2] combined with a high strength to weight ratio.

1.3 Formation of Polyurethane Foams

The general principles of urethane foam formation have already been mentioned in Fig. 1 (Section 1.0). They are based on the reaction of isocyanates with compounds containing active hydrogens. Figure 2 illustrates a typical chemical reactions that occur in the formation of polyurethane foams.

Fig 2


POLYOL
ISOCYANATE
HO
OH
+
OCN
NCO
Crosslinking agent (e.g. NH2 NH2)
-NCO + NH2
NH - C - NH
O
Blowing Agent (water, Fluorocarbon)
NCO + H2O
CO2 + NH2
in-situ blowing agent
Catalysts (t-amines & tin salts)
e.g. dimethylethanolamine &
Stannous Octoate.
Stabiliser
E.g. Silicone Copolymer
NH - C - O
O
Polyurethane

CHAPTER 2

Raw Materials

2.1 General Introduction

The urethane linkage results from the interaction of an isocyanate with a hydroxy compound:

$$R - NC\overset{\diamond}{O} + HO-R' \longrightarrow R - NH - CO - O - R \quad \text{-----(2)}$$

It is apparent that (2) leads to polyurethanes when multifunctional reactants are used. When a diisocyanate and a diol react together a linear polyurethane is obtained whilst a diisocyanate and a polyol (polyhydric compound) lead to a cross-linked polymer. A cross-linked polyurethane could also be obtained from a compound containing three or more isocyanate groups and a diol but this approach is of limited commercial importance.

Thus diisocyanates, diols and polyols are the principal raw materials used in the preparation of polyurethane foams. The more important of these

ingredients are described in the following sections.

2.2 Diols and Polyols

The earliest polyurethanes were based on aliphatic diols (glycols) such as 1, 4-butanediol. A shift has however been made to polymeric hydroxy compounds which permit the manufacture of products of wider range at relatively low cost. Polyethers and polyesters[13] are the polymeric hydroxy compounds which have received greatest attention.

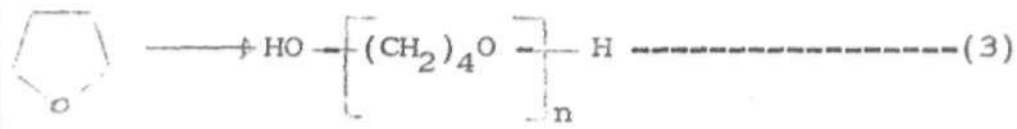
2.2. 1. Polyethers

Polyether polyols used in the preparation of flexible foams[14] generally have molecular weight in the range 3000-5000 while those used for preparing rigid[14] foams have molecular weights in the range 300-1,200. The low molecular weight polyols used for rigid foam preparation have higher number of hydroxyl groups per unit weight of polyol thus increasing the degree of crosslinking. Additionally, the decreased distance between a hydroxyl group to another contributes to the increased crosslinking.

Some of the diols and polyols used in urethane

preparation are made by the following routes:

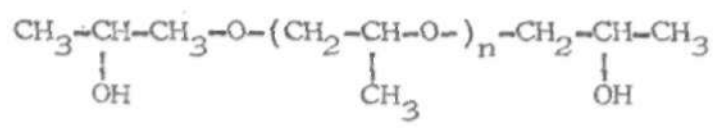
a) Tetracol: This is an expensive introduced by Du Pont. It is made by ring scission polymerization of tetrahydrofuran:



(3)

b) Polyoxyethylene glycol - This is a cheaper product than tetracol but too hydrophilic for successful use. This is prepared by ring opening polymerization of ethlene oxide.

c) Propylene oxide polyether polyols - These are prepared by ring opening polymerization of propylene oxide in the presence of propylene glycol as initiator and a caustic soda catalyst at about 160^{o}C. They are less hydrophilic than poly(oxyethylene) glycol and have a general structure:



d) Block copolymer of ethylene oxide and propylene oxide - Wyandotte Chemical (U.S.A.) introduced block copolymers of ethylene oxide and propylene oxide as a polyether polyol. This polyol under the trade name of Pluronic is less hydrophilic than poly(oxyethylene) glycol and more reactive than propylene oxide polymers.

e) Trils - Propylene oxide when catalysed by trimethylol propane, 1,2,6-hexane triol or glycol gives the following polyol

$$HO-(C_3H_6O)_n-CH_2-CH(OH)-CH_2(C_3H_6O-)_n-OH$$

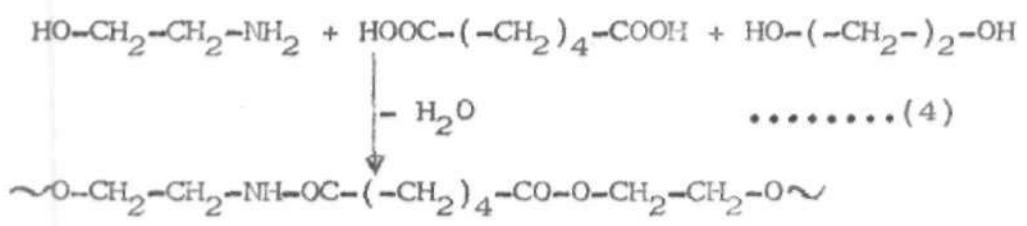
2.2.2 Polyesters

The polyesters used in the preparation of polyurethanes generally have molecular weights[13] in the range 1000-2000 and are liquids or low-melting solids. An essential feature of these polyesters is that they are hydroxyl terminated and thus hydroxyl groups are available to participate in the urethane reaction. The polyesters are prepared by the reaction of dibasic acids such as adipic acid and sebacic acid with

glycols such as ethylene and diethylene glycols or with polyhydric alcohols such as glycerol and trimethylolpropane. Depending upon the reactants used, the products range from linear polymers to highly branched polymers; the structure of the polyesters determine of course, the nature of the polyurethane foam ultimately obtained.

2.2.3 Miscellaneous polyols

Hydroxy-terminated polyesteramides are also used in the preparation of polyurethanes. A typical product may be made by the reaction of adipic acid, ethylene glycol and ethanolamine:



Polyurethanes based on polyesteramides were originally developed as elastomers but now they find use primarily as leather adhesives and flexible coatings for rubber goods.

Another hydroxy-compound used in the preparation

of polyurethanes, particularly semi-rigid foams is castor oil. It is essentially a triol composed largely of glyceryl ester of ricinoleic acid.

2.3 Di-isocyanates

Di-isocyanates are highly reactive and toxic materials. They are liquids which can affect the skin, eyes and respiratory systems. A person exposed to them may suffer from sore throats, bronchial spasms and tightness of the chest. Their respiratory effects are said to depend on their volatility.

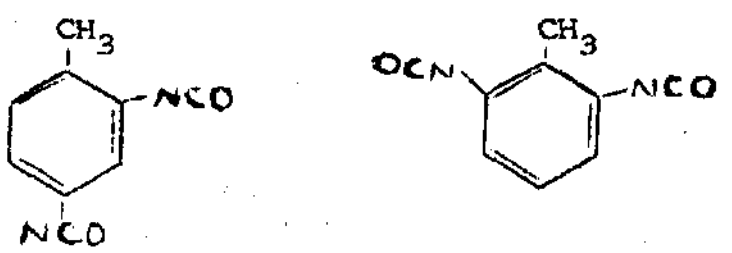
Several reactions are known by which isocyanates may be prepared. The only method of preparation which is of commercial importance is phosgenation of primary amines[15]:

$$R\text{-}NH_2 + COCl_2 \longrightarrow R\text{-}N{=}C{=}O + 2HCl \text{--------(5)}$$

The commonly used diisocyanates in polyurethane foam preparations are tolylene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI).

2.3.1 Tolylene di-isocyanate (TDI)

TDI is the di-isocyanate normally used for producing flexible polyurethane foam. It is an 80:20 (parts by weight) mixture of 2:4 and 2:6 tolylene di-isocyanates:



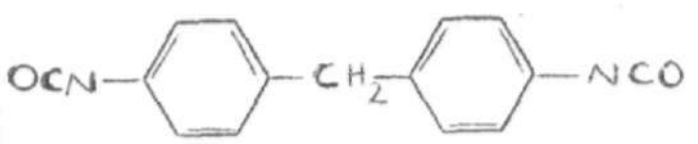
Isomers of TDI

For some uses a 65:35 mixture of TDI is used. TDI is a hazardous (toxic) chemical.

TDI is prepared by injecting toluene diamine feed into a solution of phosgene in an inert solvent such as O-dichlorobenzene at 25-100°C and then the product passed through a heater at 150-160°C. Hydrogene chloride and unreacted phosgene are taken off and the di-isocyanates separated as '80:20' TDI or '65:35' TDI.

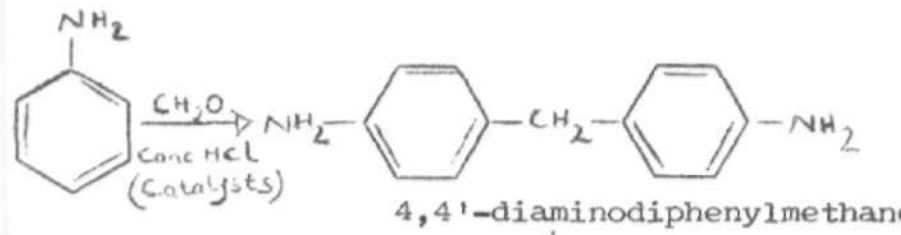
2.3.2 Diphenylmethane Di-isocyanate

Diphenylmethane di-isocyanate (MDI) is used for preparing rigid polyurethane foams it is a less toxic isocyanate and may be represented by 4,4' di-isocyanate-diphenylmethane.



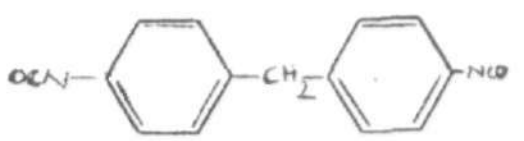
MDI

MDI is derived from aniline; the principal reactions involved are -



4,4'-diaminodiphenylmethane

$COCl_2$ (phosgenation)



diphenylmethane 4,4'-diisocyanate

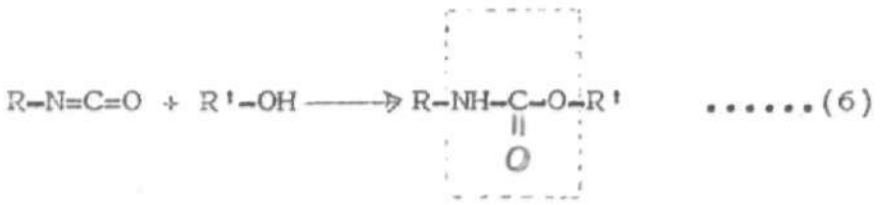
Crude MDI is a liquid while the pure form is a solid, m.p. 37-38°C. Crude MDI is employed in the preparation of rigid foams while the pure solid form is used for the manufacture of elastomers.

2.3.3 Reactions of Isocyanates with Active Hydrogen Containing Compounds

The two most important reactions in the preparation of polyurethane foams are the reactions between diisocyanates and polyols and the reaction between isocyanates and water. These reactions and other secondary reactions involved are numbered 6-15 in this section. The di-isocyanate - hydroxyl reaction (6) is the basic reaction for the formation of the urethane groups and can be considered as the chain propagating reaction. The diisocyanate - water reaction (7) is responsible for the foaming action by the liberation of carbon dioxide. The first step in this reaction is the formation of the unstable carbamic acid which decomposes to form an amine and carbon dioxide. The amine liberated in (7) immediately reacts with additional isocyanate to form a substituted urea as shown in (8).

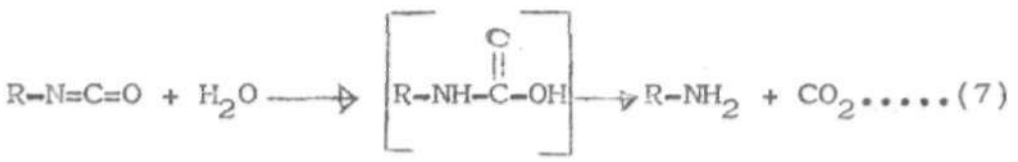
Equations (7) and (8) can be represented as in (9). An alternative[21] to (7) and (8) provides for the formation of a carbamic acid anhydride followed by decomposition to a substituted urea and carbon dioxide as shown in (10 and (11). Another reaction which may occur to some extent is the formation of an amine salt of carbamic acid which decomposes under the influence of heat to form water and urea (12).

Other secondary reactions of isocyanates which are important for crosslinking in polyurethane foam formation are the formation of allophanates (13), biuret linkages (14) and hydrolytically and thermally stable isocyanate rings (15) formed by the trimerisation of the isocyanate compound.



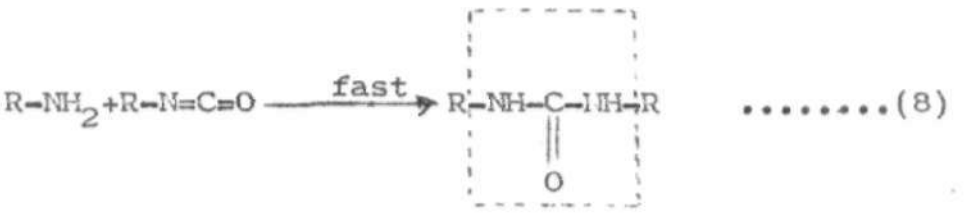
.....(6)

Urethane



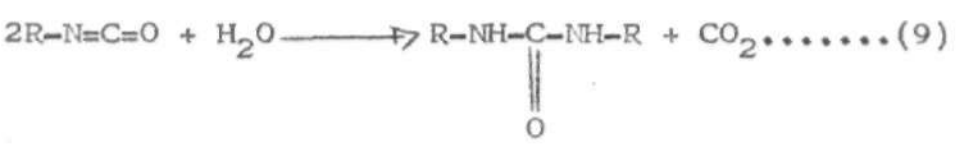
.....(7)

Carbamic Acid

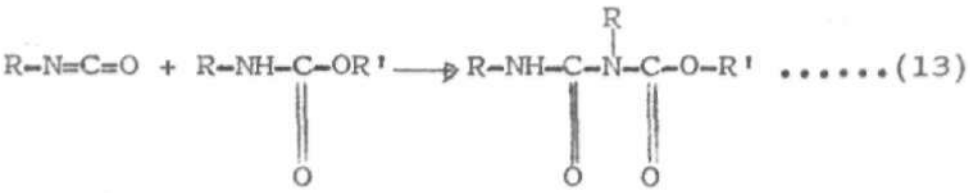


.....(8)

Urea

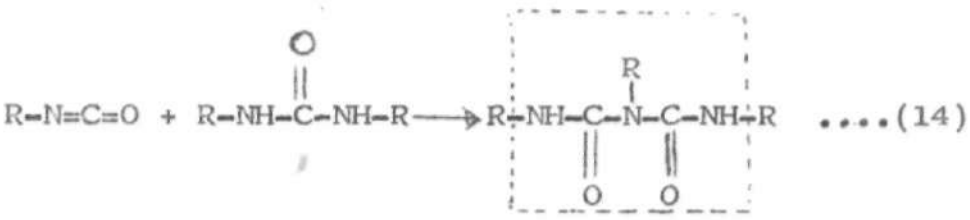


.....(9)



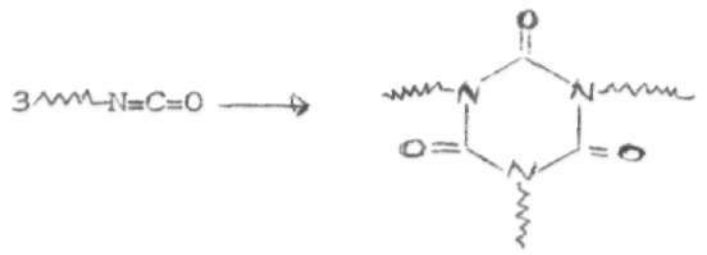
.....(13)

Allophanate



....(14)

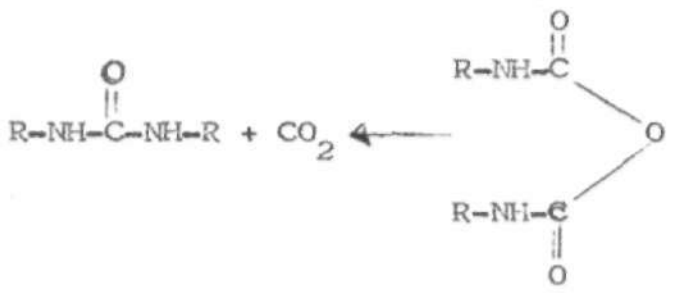
Biuret



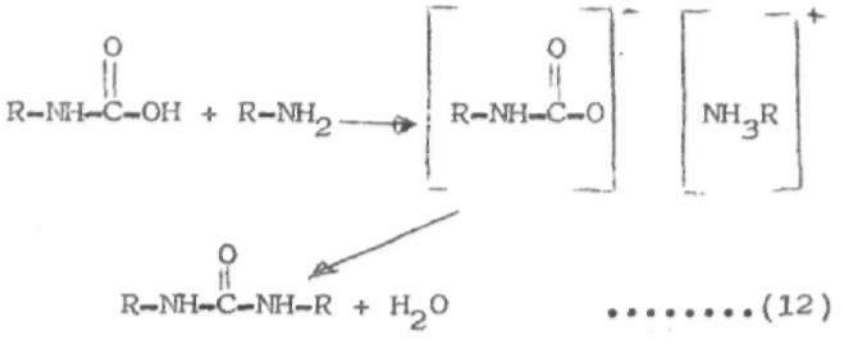
.....(15)



.....(10)



.....(11)



.....(12)

2.3.4 Effect of Substituents on the reactivity of isocyanates

The ability of the isocyanates to undergo the

reactions described varies considerably with the structure of the isocyanate.[15] Kaplan showed the effect of structure by measuring the influence of substituted phenyl isocyanates[16] with 2-ethylhexanol and found their relative activities as follows:

p - NO_2 > M - NO_2 >> M-CF_3 > M - Cl > m - Br > m - NCO > p - NCO > p - Cl > m - CH_3O > phenyl isocyanate > m - CH_3 > p - CH_3 > p - CH_3O.

m - Xylylene diisocyanate react roughly 20 times faster[15] than hexamethylene diisocyanate (HMDI) in the first step and 40 times faster in the second step.

2.4 Catalysts

Since many of the reactions shown in equations (6) - (12) are too slow for the commercial manufacture of urethane foams, catalysts whose functions are not only to bring about faster rates of reaction but also to establish a good balance between the chain propagation reaction (mainly the isocyanate-hydroxyl reaction) are employed. Another important role played by catalysts in urethane formation is to effect a completion of the reactions and thus ensure an adequate cure of the polymers.

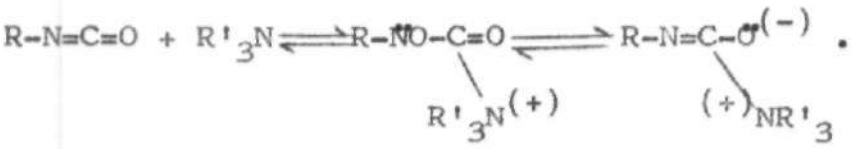
2.4.1 Amine Catalysts

The need for very fast reactions led to the development of highly active catalysts.[17] The most commonly employed catalysts in polyurethane foam formation are tertiary amines [18,19] and tin salts of fatty acids[20]. Frisch and Rumao[21] (See Table 1) have shown that the activity of amine catalysts depend upon the basicity and upon the accessibility of the nitrogen atom. Primary and Secondary aliphatic amines are not used because they react with the isocyanate to form urea derivatives which are not active enough to catalyze the reactions. Aromatic amines and amides are not effective catalysts because they

Table 1. Relative Catalytic Activity of Tertiary Amine Catalysts.

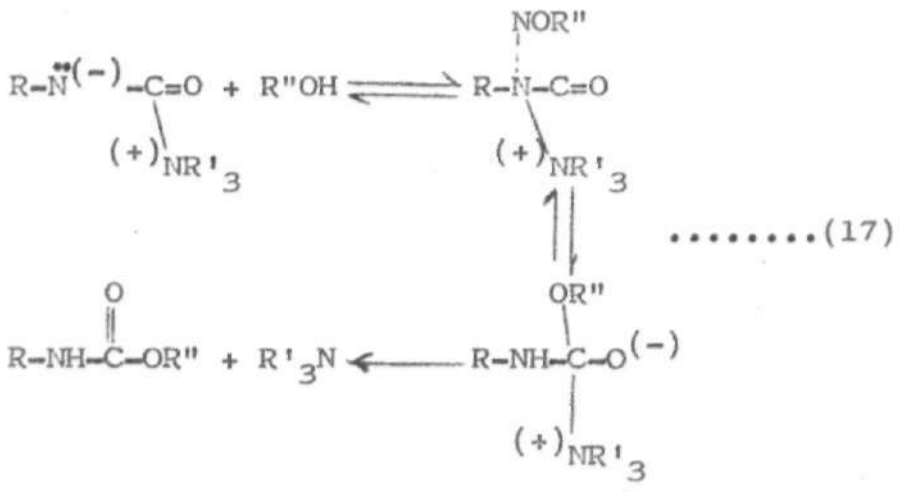
Chemical name	Pka	Relative Catalytic activity
1,4-Diazobicyclo (2,2,2)-Octane	5.4	23.9
N,N-Diethylcyclohexylamine	10.0	0.7
N-Methylmorpholine	7.4	1.0
N,N,N',N'-Tetramethyl-methane diamine	10.6	0.085
Dimethylethanolamine		

similarly are not sufficiently basic. Tertiary amine catalysts are said to catalyse isocyanate - hydroxy reaction through the formation of an intermediate complex involving both the isocyanate and the addendum[17,22]. The amine catalyst combines with the isocyanate functional group to form the reactive intermediate complex (16)



.....(16)

The electron withdrawing group on the diisocyanate molecule and the donor group on the active hydrogen compound increase the rate of the reaction. This intermediate is attacked by a second molecule of the addendum to give the urethane product shown in equation (17)



.....(17)

2.4.2. Organotin Catalysts

Organotin compounds seem to be by far the more important catalysts[20] for the isocyanate - hydroxy reaction. They include tin salts of fatty acids, tin oxides alkoxides[23,24] and phenolates. The activity of tin salts (phenolates)[25] has been compared[26] and shown in Table 2.

Gemeinhordt and Britain[27] proposed the following mechanism for catalysation by tin salts (MX_2) of the isocyanate - hydroxy reactions. The mechanism is shown in equation (18).

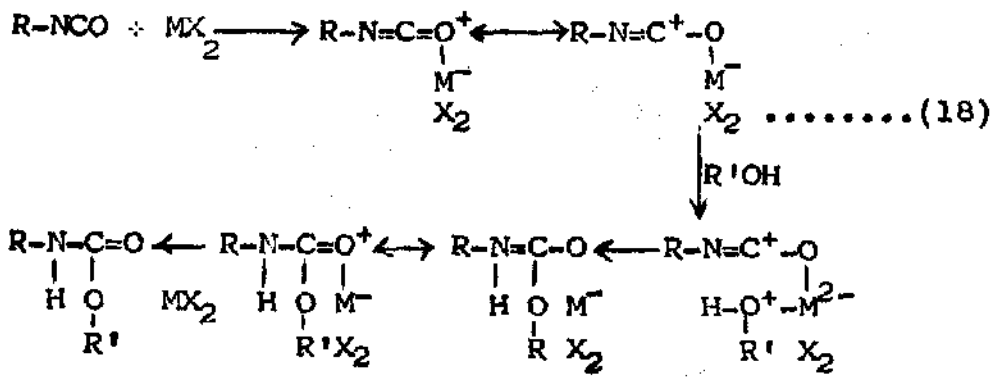
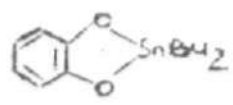
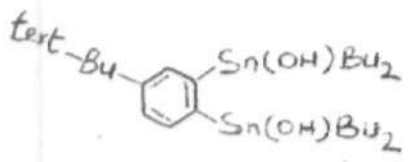
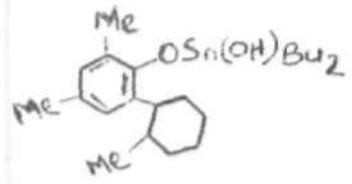
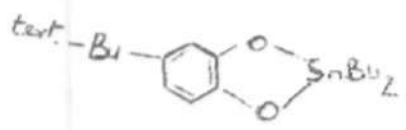
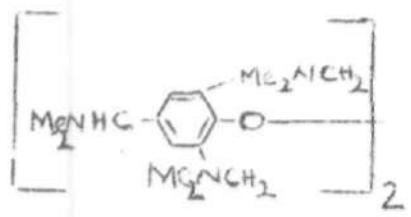


Table 2: Comparison of the activity of some of the t-amine catalysts with those of phenolates

Catalyst	Cure time (hrs)
None	20.0
Dimethylcyclohexylamine	3.0
Dimethybenzylamine	6.0
	1.5
	2.0
	1.5
	1.3
	1.5

2.4.3 Synergism of t-amine and tin salt catalysts

Some catalysts (e.g. t-amine and tin salts of fatty acids) are synergistic. That is x parts of t-amine used with y parts of tin salt of fatty acid is more effective than x + y parts of either of the catalysts used alone. Frisch and Rumao' have shown that synergism is a very important factor in the catalysis of polyurethane foam formation. It is therefore of common practice to use combinations of tertiary amines and tin catalysts together in the preparation of flexible foams and to some extent in rigid foams.

2.5 Other Ingredients in polyurethane foam preparation.

2.5.1 Blowing agents.

The blowing agents commonly used in polyurethane foam formation are carbon dioxide (an in-situ blowing agent generated by the isocyanate - water reaction) and trichlorofluoromethane (Cl_3FC) commonly called Refriegerant 11 or Freon 11. The later blowing agent which boils at 23.8^{o}C is used as an optional blowing agent. Freon is a liquid but it is easily evaporated by the

heat of reaction since it has a low boiling point. The bubbles of the carbon dioxide gas is trapped in the polymer matrix as it is formed and a cellular product results. The matching of the two processes (forming a polyurethane polymer concurrently with gas evolution) is essential for the formation of satisfactory foam products. If gas evolution is too rapid, the foam initially rises well but then collapses[13] because polymerization has not proceeded sufficiently to give a matrix strong enough to retain the gas. If polymerization is too fast, the foam does not rise adequately.

2.5.2 Foam Stabilisers.

Foam stabilisation is a complex and ill understood process. Correlation between the chemical structure of foams and stabiliser performance is difficult to deduce. However, some general rules are very well known. Silicone copolymers are made up of block copolymers of poly-dimethylsiloxane and copolymer of ethylene oxide and propylene oxide. These are the most well known stabilisers for polyurethane foam preparation. Essentially, the function of silicone copolymer is to control the cell structure in the foams.

The catastrophic effect of a low or high stabiliser content in a polyurethane foam formulation cannot be over emphasised. Low stabiliser content shoot out various troubles such as inability of foam to rise, appearance of large bubbles which burst on the surface, slow recovery when idented and foam being composed of large cells. Low stabiliser content also makes the foam to fall after rising. Wrinkles, indentations and shrinkage are caused by excess stabiliser content.

These problems are managed by increasing/decreasing stabiliser content or checking it's activity.

2.6 The Polymerization Process

Polyurethane foam can be prepared by either of two processes viz, the two stage process and the one stage process.

2.6.1 The two Stage process

The two stage process involves firstly the manufacture of the prepolymer from polyol and diisocyanate and secondly the reaction of the pre-polymer with stabiliser, water and catalysts to produce the foam. This process does not give a high throughput.

2.6.2 The One stage process

The one stage process is almost exclusively used these days because the process enables high throughputs to be achieved. As the name implies, it does not go through the pre-polymer stage unlike the two stage process described in earlier section. It only requires a thorough blend of all the ingredients except the di-isocyanate which is added only when a good blend is obtained. Mixing is continued on addition of isocyanate for about 8-10 seconds. The foam is then allowed to form either in a mould or on an appropriate support by transfering the mixed ingredients while still in liquid form.

2.6.3 Industrial process

In industry, the process of polyurethane foam preparation essentially comprises the mixing together of the raw materials in an enclosed mixing head in such a way that thorough mixing is achieved. The resultant mixture is discharged in the liquid state onto a moving belt or into a mould where foaming occurs.

On slabstock machines, the complete mixing head

usually traverses the width of the conveyor belt. This results in the liquid being laid down in a series of lines at small alternate angles to one another. Paper is fed continuously to line the conveyor belt and the side walls. Also the moving conveyor belt slopes away from the mixing head at an angle of 2-6 degrees to the horizontal to ensure that the liquid mix being dispensed onto the belt does not fall onto material which has already started to foam.

CHAPTER 3

Scope of Present Investigation

In Nigeria there are very many foam manufacturing units. Their products are at the moment used in comfort cushioning, general upholstery and door panels.

These units strictly follow the standard recipes supplied by the manufacturers of the raw materials without any regard to varied demands of their consumers. They have been able to get along without difficulty because Nigeria has at the moment not set up a products standard board in this field and also because the markets for these products are nowhere near saturation.

The present investigation was therefore conducted to understand the effect of variation of composition of polyurethane formulation on the physical properties of foam obtained. A clear understanding of this behaviour is essential to produce foams of desired properties.

The following investigation were then carried out in this study:

(a) Flexible polyurethane foams.

1) Effect of variation of Tolylene diisocyanate proportion on the physical properties of foam.
2) Control of evolution of carbon dioxide in polyurethane foam formation.
3) Effect of mixed blowing agents on the physical properties of foam.
4) Effect of rise height of foam on its properties.
5) Load - Compression behaviour of some flexible polyurethane foams.

(b) Rigid polyurethane foam:

With the growth of the refrigeration industry where rigid foams are used as insulators and the future growth expected in their use in road construction, the following studies were carried out for rigid foams:

1) Effect of blowing agent concentration and hence density on Load-Compression behaviour of rigid foams.

2) Effect of blowing agent concentration on the thermal conductivity of rigid foams.

CHAPTER 4

EXPERIMENTAL

4.1 Materials

The various specifications of raw materials used in the preparation of polyurethanes are all of commercial grades and are listed below:

1. Polyol - The polyols used are polyether triols (shell urethane Chemicals) of molecular weight 3000 - 3500 for flexible foams and lower molecular weight polyols (300-1200) for rigid foams.
2. Di-isocyanates - The di-isocyanate used is an 80:20 (parts by weight) mixture of 2:4 and 2:6 tolylene di-isocyanates (TDI).
3. Catalysts - Two synergistic catalysts were used viz:
   i. Dimethylethanolamine.
   ii. Stannous Octoate.
4. Two blowing agents - Two catalysts were used:
   i. Water - an in-situ blowing agent.

ii. Freon 11 - an auxiliary blowing agent (b.p. $23.8^{o}C$).

5. Surfactant - The surfactant used is a silicone copolymer (Union Carbide Chemical Co.).

6. Other chemicals used were of AR grades.

4.1.1 Storage of Chemicals

Special care has to be taken in the storage of polyether triols (polyol) and tolylene di-isocyanate (TDI) because of the hygroscopic nature of polyol and high reactivity of TDI.

Polyol must therefore be stored under air tight conditions so that contamination with water and absorption of moisture from the atmosphere are prevented.

TDI on the other hand shows a high reactivity with water. Because of the low equivalent weight of water, a slight trace of it reacts with quite a lot of isocyanate. Moisture from techniques employed results in the formation of insoluble ureas - as shown in equation (19) below:

$$2RN=C=O + H_2O \longrightarrow RNHCONHR + CO_2 \quad \ldots\ldots\ldots\ldots(19)$$

Another problem in the storage of isocyanates is that they are facile to dimerization[28] even in the absence of catalysts. This problem can be slowed down by storage at lower temperatures [29, 30]. Finally, though trichlorofluoromethane (Refrigerant or Freon 11) is inert, it boils at 23.8°C and has to be stored in the refrigerator. Even when in the refrigerator, care should be taken not to allow the Freon 11 to evaporate because it corrodes the metal as well as some plastic parts of the refrigerator.

4.1.2 Handling Precautions

Polyol has a low order of toxicity. Normal care should however, be taken to avoid unnecessary contacts.

Isocyanates on the other hand are in general toxic and care must be exercised in handling them. Inhalation of isocyanate vapours can be very dangerous. Tolylene di-isocyanate (though non-volatile) evaporates very quickly if spilled on the bench and causes irritation of the eyes.

4.2 Preparation of Flexible Polyurethane Foam[31]

4.2.1 Principle

The carbon dioxide produced when water reacts with TDI as shown in equation (7) expand the foam to give a porous white solid consisting of many small pores. This happens because the carbon dioxide bubbles cannot escape because of the rapidly increasing viscosity of the reaction medium.

A typical formulation for the preparation of flexible polyurethane foam is given in Table 3.

4.2.2 Procedure

Glass containers are unsuitable for flexible foam preparation because cured foams stick to glass.

Table 3: Typical formulation of flexible foam preparation.

Ingredients	Millimoles	Parts by weight
Polyol	-	100
Tolylene di-isocyanate	230	40
Water	166.7	3
Dimethylethanolamine	6.7	0.6
Stannous Octoate	0.7	0.3
Silicone	-	1.0

A polythene lined paper cup is most suitable for flexible foam preparation. The recipe used for a 190 cm^3 paper cup is given in Table 4.

Table 4: Flexible foam recipe for a 190cm^3 paper Cup.

Ingredients	Millimoles	Parts by weight
Polyol	—	10
Tolylene di-isocyanate	23.0	4
Water	16.7	0.3
Dimethylethanolamine	0.67	0.06
Stannous Octoate	0.07	0.03
Silicone Copolymer	0.10	0.10

All the ingredients except TDI were transfered into a 190 cm^3 paper cup and very thoroughly blended with a magnetic stirrer. After a thorough blend was obtained, the 4.0g of TDI previously conditioned to a temperature of 19-20^oC was next introduced into the cup and mixing continued for another 20-30 seconds after which the stirrer was quickly removed with the help of a pair of forceps. All the liquid ingredients apart from polyol and TDI were measured with micro pipettes Polyol and TDI were weighed accurately using a metler balance.

4.3 Variation of the proportion of Tolylene diisocyanate (TDI) in flexible polyurethane foam preparation.

Polyol and Tolylene di-isocyanate (TDI) are the two main ingredients of flexible polyurethane foam preparation. The effect of their proportion on the physical properties of flexible foam was investigated.

4.3.1 Procedure

This investigation was carried out by varying the TDI concentration in the formulation while keeping the concentration of all other ingredients constant. The normal procedure and precautions described in section 4.2 were taken. TDI concentration was varied from 23.00 milimoles to 31.09 milimoles. The foams so prepared were labelled F_1 - F_5 as shown in Table 5.

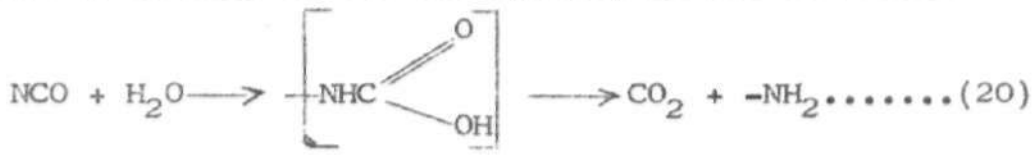
Table 5: Variation of TDI concentration in flexible foam formulation.

Serial No.	TDI Concentration (milimoles)
F_1	23.00
F_2	25.30
F_3	27.60
F_4	29.90
F_5	31.04

4.4 Control in the rate of evolution of Carbon dioxide

4.4.1 Aim

Since some of the carbon dioxide formed during the foaming may be lost to the atmosphere, it was therefore



(20)

though that it would be of commercial importance if this is prevented. An attempt at preventing this loss of carbon dioxide was made by controlling the rate of evolution of carbon dioxide by adding varying amounts of 1 M sodium hydroxide to the flexible polyurethane foam formulation.

4.4.2 Procedure

In this investigation, varying amounts of 1M sodium hydroxide solution was added to the standard recipe (See Table 4). The amount of sodium hydroxide solution added was varied from 0-4.70 cm^3. The experiment was repeated without the addition of the normal 0.30 cm^3 of water used in flexible foam preparation. The foams were prepared as described in section 4.2 and the

time for foam to rise to it's maximum height was recorded in each case. The experiment was again repeated with a lower concentration sodium hydroxide solution (0.05M) and a weaker alkali - sodium bicarbonate.

4.5 Mixed Blowing Agents In Flexible Polyurethane foam preparations.

In addition to the 16.7 milimoles (0.30 cm^3) of water used in flexible urethane foam preparation, additional blowing agent (Freon 11) was used. The amount of freon 11 was varied from 1.16-9.28 milimoles. Great care was taken to avoid of freon vapour due to evaporation. The container was left in ice bath until one was ready to add it. The foams were labelled F_6-F_9 as shown in Table 5:

Table 6: Variation of Freon content in flexible foam formulation (water = 16.7 milimoles)

S/No	Amount of freon (millimoles)
F_6	1.16
F_7	2.32
F_8	4.64
F_9	9.28

Another set of flexible urethane foam were made in exactly the same manner as F_6-F_9 but using 11.1 milimoles of water (0.20 cm^3) instead of 0.30 cm^3 of water. The foams were labelled F_{10}-F_{13} as shown in Table 7:

Table 7: Variation of freon content inflexible foam formulation (water = 11.1 milimoles)

S/No	Amount of freon (millimoles)
F_{10}	1.16
F_{11}	2.32
F_{12}	4.64
F_{13}	9.28

4.6 Effect of rise height on properties of flexible polyurethane foam

4.6.1 Objective

The surface of flexible polyurethane foam sometimes peels off after cure, possible because of the fact that a bubble of gas as it rises from the bottom of a liquid to the surface increases in size. The size of the gas bubble determines the cell size and hence various physical properties of the foam. This effect was investigated by using four wooden moulds of different dimensions thus giving foams of varying heights.

4.6.2 Procedure

A thorough blend of the normal ingredients of flexible polyurethane foam (Table 4 doubled) was transfered from the paper cup to the wooden mould and foam allowed to rise undisturbed. The experiment was repeated with exactly same quantity and proportions of the ingredients in the other three moulds.

The foams prepared were labelled F_{14}-F_{17} and their cross-sectional areas and heights measured. The physical properties

of F_{14}-F_{17} were also investigated.

4.7 Preparation of Rigid Polyurethane Foam[32,33]

4.7.1 Principle

The principle of rigid polyurethane foam is more or less the same as for the flexible foam except that while the blowing agent in flexible foam preparation can be generated in-situ by the reaction of TDI with water, rigid foam preparation requires an auxilliary blowing agent such as Freon 11 to give satisfactory properties.

A typical formulation of rigid foam preparation is given in Table 8.

Table 8: Rigid polyurethane foam recipe

Ingredient*	Parts by weight
Polyether polyol	100
Freon 11 ($CFCl_3$)	35
4,4'di-isocyanate-diphenyl-methane (MDI)	115

* Commercial grade contains all other ingredients in appropriate amounts.

In this investigation, a commercial grade of polyol (functionality greater than 3 and molecular weight of the order of 300-1200) obtained from a local manufacturer and containing appropriate amounts of flame retardant, tertiary amine catalyst and silicone copolymer was used.

4.7.2 Procedure

10.0g of the polyol containing appropriate amounts of stabiliser, flame retardant and catalyst was thoroughly mixed with 11.5g of 4,4'-di-isocyanate diphenylmethane (MDI) and 3.5g of Freon 11 in a paper cup. The blended viscous liquid was quickly transfered into a cylindrical aluminium mould lined with polythene sheet. The bottom part of the aluminium mould is removable while the top is open so that the cured rigid foam could be removed with ease.

4.7.3 Effect of Freon concentration on rigid polyurethane foam properties

This investigation was carried out by preparing four samples of rigid foams containing between 1.16-9.28 milimoles of Freon 11 using the procedure described

under section 4.7.2. The amount of Freon used in each case were labelled R_1-R_4 as shown in Table 9.

Table 9: Variation of Freon content in rigid foam formulation.

S/No	Freon content (milimoles)
R_1	1.16
R_2	2.32
R_3	4.64
R_4	9.28

4.8 Density Determination[34]

Density is one of the fundamental properties of polyurethane foams. It is very informative as a measure of the weight incurred in using a particular foam. It is related porousity, solid content and hence cost.

The foams were cut using electric saw and dimensions measured accurately using calipers after which the samples were weighed accurately. The volume was determined from the dimensions and thus density calculated from the mass and volume of respective foam samples.

4.9 Tensile Properties

4.9.1 Theory

The most common type of stress - strain measurement is made in tension, that is by stretching the material. The stress at break is given by

$$= \quad = F/A \quad .....(21)$$

where F = force at break

A = cross sectional area at failure

However, for experimental convenience, most tensile strenghts are based on the original cross section A_1 since this is easily measurable before the test is started.

If this tensile stress indices an extension of x, then the tensile strain is defined by

$$\sigma_1 = \frac{x}{\text{length of specimen}}$$

The percentage strain at any given extension is defined by

$$\sigma_2 = \frac{\text{Extension}}{\text{Original length}} \times \frac{100}{1} \quad .....(22)$$

4.9.2 Tensile Measurement

The Instron model 1026 was used in studing the tensile properties of the flexible foams prepared. The instrument has a maximum capacity load weighing system of 500 kg and a minimum capacity of 1 gm hence a weighing range of 1gm - 500 kg.

Test speeds are selected by changing gears. The normal test speeds are 50, 100, 200, 500 mm/min to 200kg capacity and 50, 100 and 200 mm/min to 500 kg capacity. Tensile measurements were made at a constant rate of strain. The strain obtained can either be magnified or reduced by adjusting the chart speed.

In this study the ranges selected are:- Tension cell 1026 BM with a tension load range of 1-2000 gm, cross-head speed 100 mm/min and chart-time speed of 100 mm/min.

Some of the various parameters encountered in the treatment of data are collected and defined in appendix 1.

4.9.3 Procedure

The samples tested were conditioned to 25^{o}C and 65% relative humidity. The American standard test method

(ASTM) for preparing samples for test in an Instron was used for the flexible foams tested. The method requires a dumbbell shaped test piece. The gauge length of the test pieces were adjusted to 2.5-5.00 cm. The thickness of the test pieces and the width were always measured accurately with a micrometer screw gauge. The sample was then clamped between the jaws of the Instron Clamp and a load extension curve recorded automatically from where the load at break and extension at break were noted. The stress and the corresponding % elongation were calculated as follows:

$$\text{Stress} = \frac{\text{Load (Kg)}}{\text{Cross Sectional area } (m^2)} \quad \ldots\ldots(23)$$

The stresses were expressed in gravitational Newtons per metre squared.

$$\% \text{ Extension} = \frac{\text{Elongation}}{\text{Magnification factor}} \times \frac{1}{\text{gauge length}} \times \frac{100}{1} \quad \ldots.(24)$$

Since the cross-head speed and chart time speed were the same, the magnifaction factor is 1 so that the extensions is as recorded on chart. So the % extension is simply given as:

$$\% \text{ Extension} = \frac{\text{Elongation}}{\text{gauge length}} \times \frac{100}{1} \quad \ldots\ldots\ldots(25)$$

The typical stress-strain curves obtained for F_1-F_{17} are shown in Figs 5, 10, 11 and 15 while their tensile strengths and elongation at break are given in Tables 11, 14 and 16.

4.10 Compression behaviour of polyurethane foams

4.10.1 Machine, Test Specimen and Techniques

When two equal and opposite colinear forces are applied to a material, a compressive stress is set up and a compressive strain in every way analogous to the conditions of tensile stress and strain described earlier results. The only difference is that the compressive strain is in the opposite direction.

The most informative data one can obtain to characterize the compressive behaviour of a flexible foam is the entire load-compression curve and the return curve[35]. This is particularly of importance in comfort cushioning.

A W type Tensometer was used for determining the compressive behaviour of some foam samples. A 62.5 lb (28.13 kg) capacity load beam was employed for tests which were made at a constant rate of strain of 12.5 mm/min.

Compressive tests were done on four representative samples of flexible foams (F_{10}-F_{13}) and four rigid foams samples (R_1-R_4). All the samples were cut to uniform cross-sectional area of 9.00 cm^2. The thickness of each sample was measured accurately with calipers.

During the tests, special care was taken to make sure that the opposing forces were truely axial. Once the sample was axially placed, the motor was started and at the end of each compression, the motor was put on the reverse to obtain the return curve both of which are plotted automatically. The load-compression % curves for F_{10}- F_{13} and R_1-R_4 are shown in Figs 17 and 20. The load-compression % relationship for the samples of flexible and rigid foams are shown in Tables 18 and 22.

4.10.2 Characterisation of Load-Compression % Curves

In view of the non-linearity of the Load-Compression curves shown in figs 17 & 20, The characterisation of the S-shaped curves were done by the method of Carey and Rogers [2, 36-38] who defined Yield Index as the ratio of the load required to produce 50% compression to that required to produce 10% compression. On the other hand, Step Factor[36] is defined as 2 minus the ratio of load

required to produce 40% compression to that required to produce 20%. The Yield indices and Step Factors for F_{10}-F_{13} and R_1-R_4 are shown in Tables 19 and 23.

4.11 Thermal Conductivity of Rigid Polyurethane Foam[39]

Principle: An arrangement[12] designed to simulate a solution of the differential equation defining the flow of heat in a solid has been employed in this study. The derivation of the differential equation (theoretical analyses) governing the temperature distribution through the rigid foam is given in reference 39.

4.11.1 Apparatus:

1. A box made of plywood whose inside was lined with aluminium foil and its outside insulated by gluing asbestos slab onto it. The box is also provided with a similarly insulated lid which can be clamped onto the main part of the box by a bolt and wingnut device. The inner part of the lid carries a lamp holder to which an electric lamp can be fixed. On one side of the box is a hole of about 6mm to allow thermocouples into the box.

Detailed Box Dimension and the equipment used are described below.

a) Thickness - 19 mm

b) Internal dimensions - 115mm x 115mm x 213mm

c) External dimensions - 159mm x 159mm x 257mm

d) Window dimension - 98mm x 200mm

e) Dept. of Window grooves - 8mm(on top)and 9mm (on the bottom)

2. (0-200W) Wattmeter

3. (0-1A) Ammeter.

4. 140 rheostat

5. 40W, 60W, 100W and 150W electric lamps.

6. Copper-Constantan thermocouples.

7. A thermocouple potentiometer

8. Steel rule and micrometer-screw guage.

9. Two copper plates of dimension 217mm x190mm.

4.11.2 Specimens

The specimens were uniformly cut samples of R_1, R_2 R_3 and R_4 of dimensions 217mm x 100mm but not necessarily of same thicknesses.

4.11.3 Procedure

The apparatus was set up as shown in the circuit diagram in Fig. 3.

Calibration - Even though the box was properly insulated, heat losses could still be significant. It was therefore necessary to calibrate for heat losses. This was done by using an asbestos specimen of known thermal conductivity. The rate of heat loss was obtained by substracting the actual rate of heat flow(q_s) through the specimen from the measured rate of heat flow (q_m) to give the heat loss (q_l) from a fixed side of the box.

$$q_l = q_m - q_s \qquad \text{.....(26)}$$

Thus, the rate of heat loss was found at various temperature differences across a fixed side of the box. A graph of q_l against the temperature difference across a fixed side of the box is the calibration curve.

4.11.4 Temperature difference across foam samples

Each of the rigid foam sample was sandwiched between two copper plates and inserted into the grooves of the window of the box. Heat flow was allowed through the specimens by heating with the electric lamps in turn.

FIG 3

SPECIMEN
THERMO-COUPLES
ELECTRIC LAMP
THERMO-COUPLE
THERMO-COUPLES
A
AMMETER
(0-1A)
RHEOSTAT
(140Ω)
A.C
220
V
WATTMETER
(0-200 W)

The temperature difference across each sample and a fixed side of the box for each lamp used were read off from the potentiometer and recorded. Power measurements were normally taken from the wattmeter. Apart from using electric lamps to vary power dissipation, the rheostat could be also be used.

The results of these experiments are given in tables 24 - 28.

Sample Calculations

The heat loss through the asbestos cement board used for calibration was calculated for various temperature differences were calculated by substituting for thermal conductivity (K), area (in metres), thickness of sample (L) and temperature difference (DTs ^{o}K) in the equation

$$q_s = KA \frac{DTs}{L} \quad \text{.....(27)}$$

For the asbestos board cement,

$$K = 0.744 \ W/m^{o}K$$

$$A = 0.0195 \ m^2$$

$$L = 0.0125 \ m$$

$$\therefore \ q_s = 0.744 \times 0.0195 \times \frac{DTs}{0.0125}$$

$$q_s = 1.1606\ DTs$$

when DTs = 14.0 ^{o}K,

$$q_s = 1.1606 \times 14.0$$

$$= 23.75.$$

The heat loss for a temperature difference of 14.0 ^{o}K and measured heat flow (q_m) of 40W, we have from the relation

$$q_l = q_m - q_s$$

$$q_l = 40 - 23.75$$

$$= 16.25\ W$$

Thus q_l was calculated for various temperature differences and plotted against ΔTb as shown in Fig 23.

For the rigid foam samples, $q_l{}^s$ were read off from the calibration curves since the temperature difference (ΔTb) for the rigid foam samples were equally measured. From the equation $q_s = q_m - q_l$ .....(28) The heat flow (q_s) through each sample was calculated by substitution of known values into equation (28) and plotted against the temperature differences (ΔTs) across the foam samples. A straight line of best fit was drawn through the set of points for each specimen as shown in Fig 24. From the equation $K = \frac{mL}{A}$ .....(29) Hence from the slopes of the graphs K was calculated for each of R_1,R_2,R_3 and R_4 as shown in Table 29.

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CHAPTER 5

Results and Discussions

5.1 The effect of variation of TDI proportion in flexible polyurethane foam on it's physical properties.

The effect of the variation of the proportion of TDI in flexible polyurethane foam formulation on it's various properties is presented in Table 10.

5.1.1 Effect of TDI variation on Density

As can be seen from Table 10 the density of flexible polyurethane foams F_1-F_5 decreases with increase in TDI concentration. At first sight, it would appear that this trend is unreasonable when one considers that the concentration of water (in-situ blowing agent) is not increased along with TDI. As the excess TDI is added one should have expected an increase in density but the reverse is the case. When one takes the moisture content of the polyol (0.091) into account one find that the blowing agent concentration has to increase and hence responsible for the decrease of the flexible foam densities with increase in TDI concentration. The extra

Table 10

The effect of variation of TDI proportion in flexible polyurethane foam on its physical properties.

Composition of Ingredients: Polyol = 2.5 milimoles Water = 16.7 milimdes, Stannous Octoate = 0.07 milimoles, Dimethylethanolamine = 0.67 milimoles and Silicone Copolymer = 0.10g.

S/No of sample	TDI Concentration milimoles	Density Kgm^{-3}	Tensile strength at break x_{10}^{-4} GNm^{-2}	% Elongation at break % E
F_1	23.00	32.14	8.31	114
F_2	25.30	29.90	7.72	202
F_3	27.60	27.20	7.35	229
F_4	29.90	25.40	6.62	260
F_5	31.04	25.55	-	-

0.009g per 10g of polyol (0.50 milimoles) of water reacted with the excess TDI until finally when all the water had been used up. This would automatically increase the concentration of the Carbon dioxide (in-situ blowing agent). This explains the gradual decrease in density with TDI concentration. If moisture free polyol was used, there probably would not have been any pronounced effect of increasing TDI concentration on flexible polyurethane foam densities.

This shows that the original TDI concentration was not optimum. There was still excess water present in the formulation which reacted with excess TDI. Polyol was therefore analysed for moisture content. It was found to have 0.09% of water which is equivalent to 0.50 milimoles of TDI in 10g of polyol. With this extra water which was responsible for the decrease in the densities with increase in TDI concentration until about 29.90 milimoles of TDI was added when the density value went minimum, further increase in TDI didn't have much effect.

It can also be seen from Figure 4 that the density decreases linearly with TDI concentration up to 29.90 milimoles of TDI after which there is a leveling.

5.1.2 Tensile properties of flexible foams F_1-F_4

Tensile properties of Foams F_1-F_4 were investigated and given in Table 11 while Figure 5 illustrates the stress - strain characteristics of these foams.

As can be seen from Figure 5, the initial slope of the curves and hence initial modulus decreased with increase in TDI concentration. It can also be seen that the load and hence the tensile stress based on initial cross-sectional area at break goes on decreasing with increasing TDI concentration while the elongation and hence % strain increases with increase in TDI concentration. Values of stresses and % strain at break of the foams F_1-F_4 are given in Table 11 while Figures 6 and 7 show the effect of density on tensile stress and % elongation of foams F_1-F_4 respectively. As stated earlier the effect of addition of TDI is to decrease the density of the foams up to a certain minimum while Figs. 6 and 7 correlate the effect of density on tensile stress

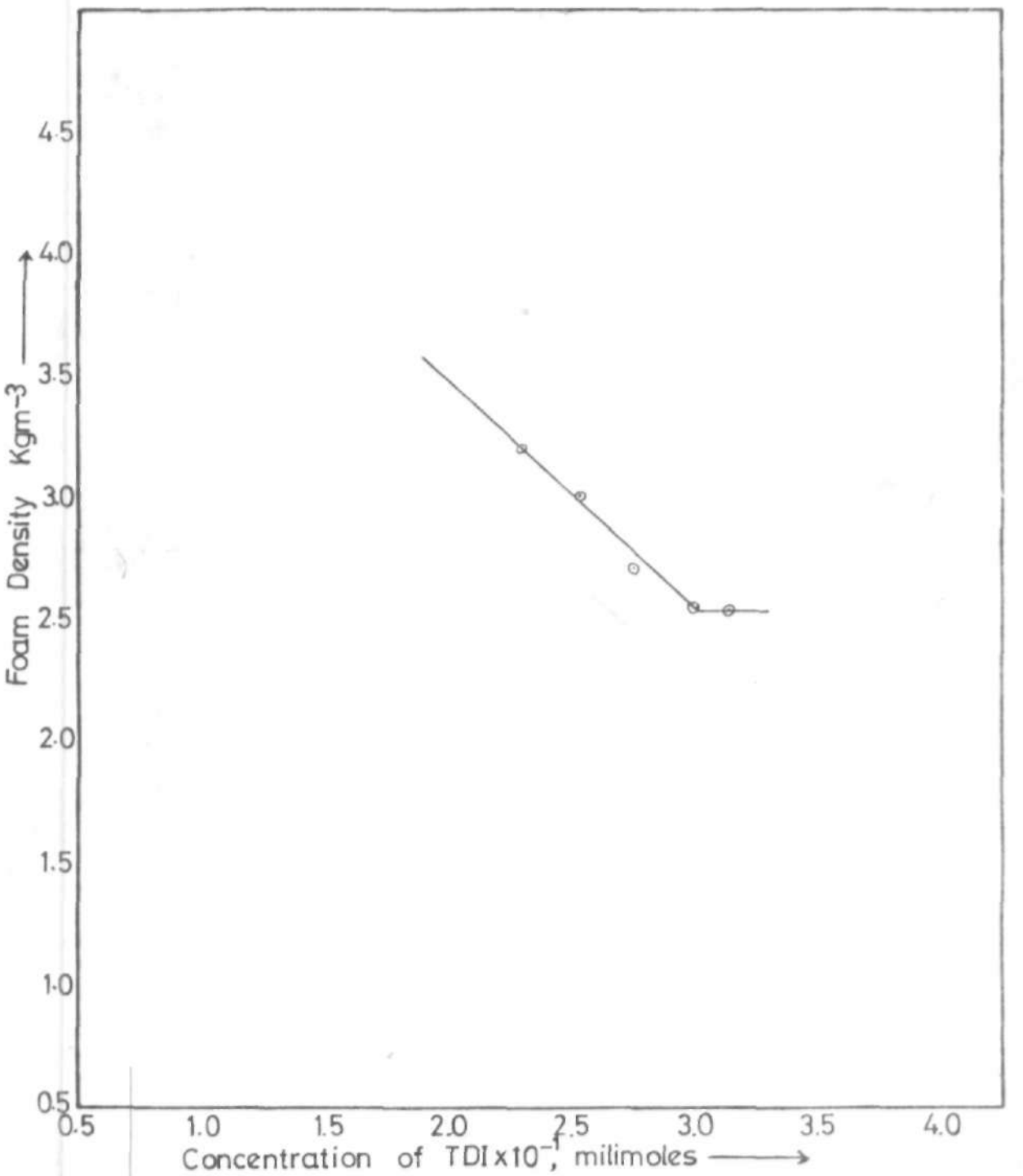


Fig 4 Effects of TDI Concentration on Density of Flexible Polyurethane Foam

Table 11

Stress - strain relationship for flexible polyurethane foams of varying proportion of TDI

(a) TDI = 23.0 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.45	9.0	0.78
100	0.80	16.0	1.56
150	1.10	22.0	2.34
200	1.45	29.0	3.12
250	1.80	36.0	3.90
300	2.20	44.0	4.68
350	2.75	55.0	5.46
400	3.45	69.0	6.24
450	4.10	82.0	7.02
500	4.95	99.0	7.80
533	5.70	114.0	8.31

(b) TDI = 25.3 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} CNm^{-2}
50	0.55	11.0	0.62
100	1.00	20.0	1.24
150	1.40	28.0	1.85
200	1.80	36.0	2.45
250	2.30	46.0	3.09
300	2.85	57.0	3.71
350	3.55	71.0	4.33
400	4.40	88.0	4.94
450	5.50	110.0	5.56
500	6.60	132.0	6.18
550	8.00	160.0	6.80
600	9.60	192.0	7.42
625	10.10	202.0	7.72

(c) TDI = 27.60 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.75	15	0.64
100	1.20	24	1.29
150	1.60	32	1.93
200	2.05	41	2.58
250	2.65	53	3.22
300	3.40	68	3.87
350	4.35	87	4.51
400	5.50	110	5.16
450	6.90	138	5.80
500	8.55	170	6.44
550	10.60	212	7.09
570	11.45	229	7.35

(d) TDI = 29.90 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.30	12	0.53
100	0.60	24	1.07
150	0.85	34	1.60
200	1.10	44	2.14
250	1.45	58	2.67
300	1.90	76	3.20
350	2.45	98	3.74
400	3.15	126	4.27
450	4.00	160	4.80
500	4.95	198	5.34
550	6.00	240	5.87
600	7.00	280	6.62

at break and % elongation at break of foams F_1-F_4

The decrease in tensile stress with increase in TDI concentration is due to the more porous structures formed with increased blowing agent concentration brought about by the reaction of the excess TDI with the moisture content of the polyol used. The extra porous structures resulted from increased concentration of in-situ blowing agent. These porous structures are bound to affect the cross-linking density by decreasing it. Since the cross-link density in polyurethane foams play a major role in their strengths, it is no wonder that the tensile strength at break decreased with decrease in density.

Fig. 7 shows that % elongation at break rises steeply with decrease in flexible foam density. As stated above the porousity of foams increase with decrease in density and hence one would observe the increase in % elongation - with decrease in density. The decreased cross-link density with decreasing density also explains the inverse relationship observed here since a given load is bound to produce a larger elongation in a flexible foam of lower density than for one

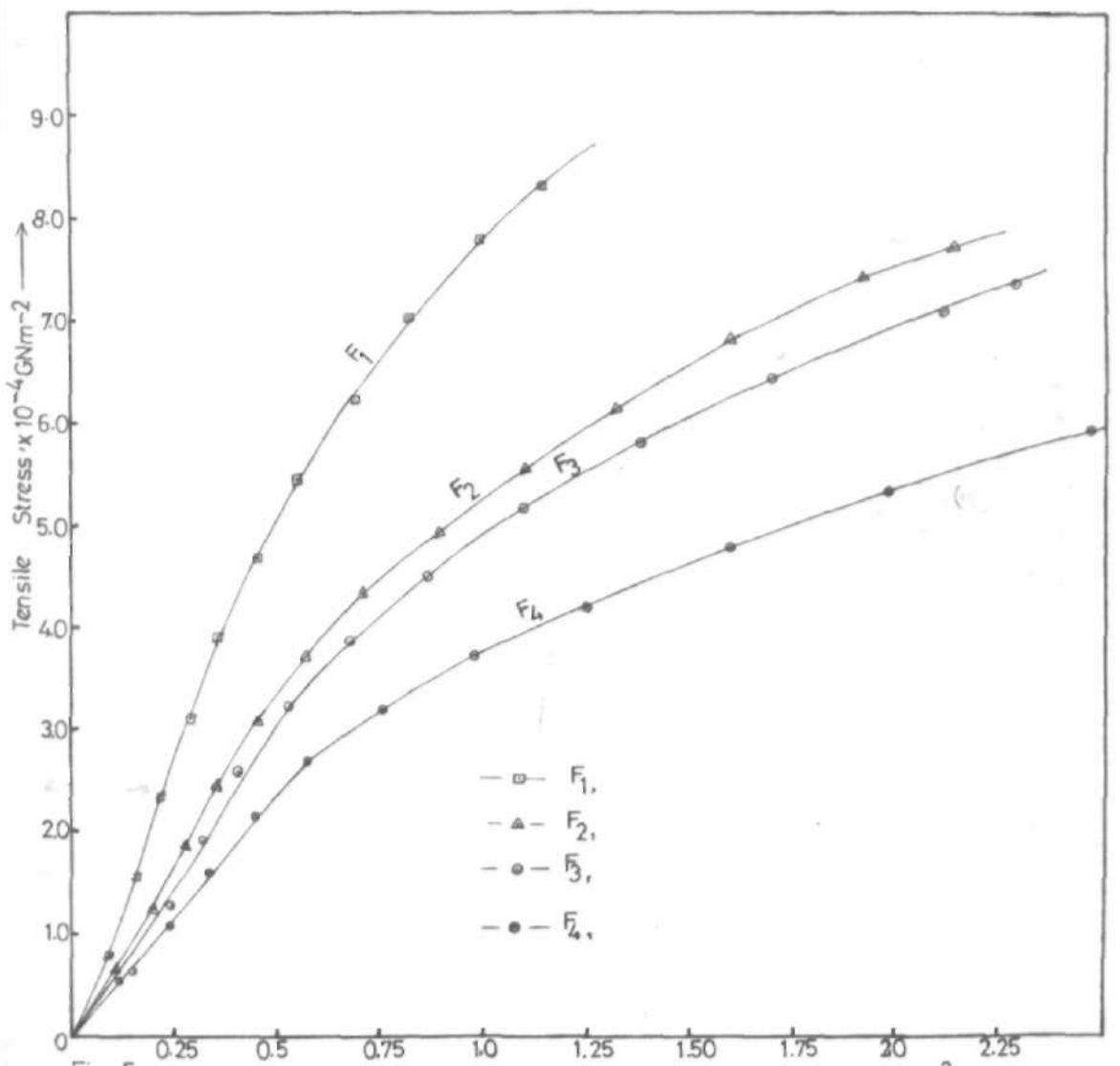


Fig 5
Stress–Strain Relationship for Flexible Polyurethane Varyiny Proportion of TDI

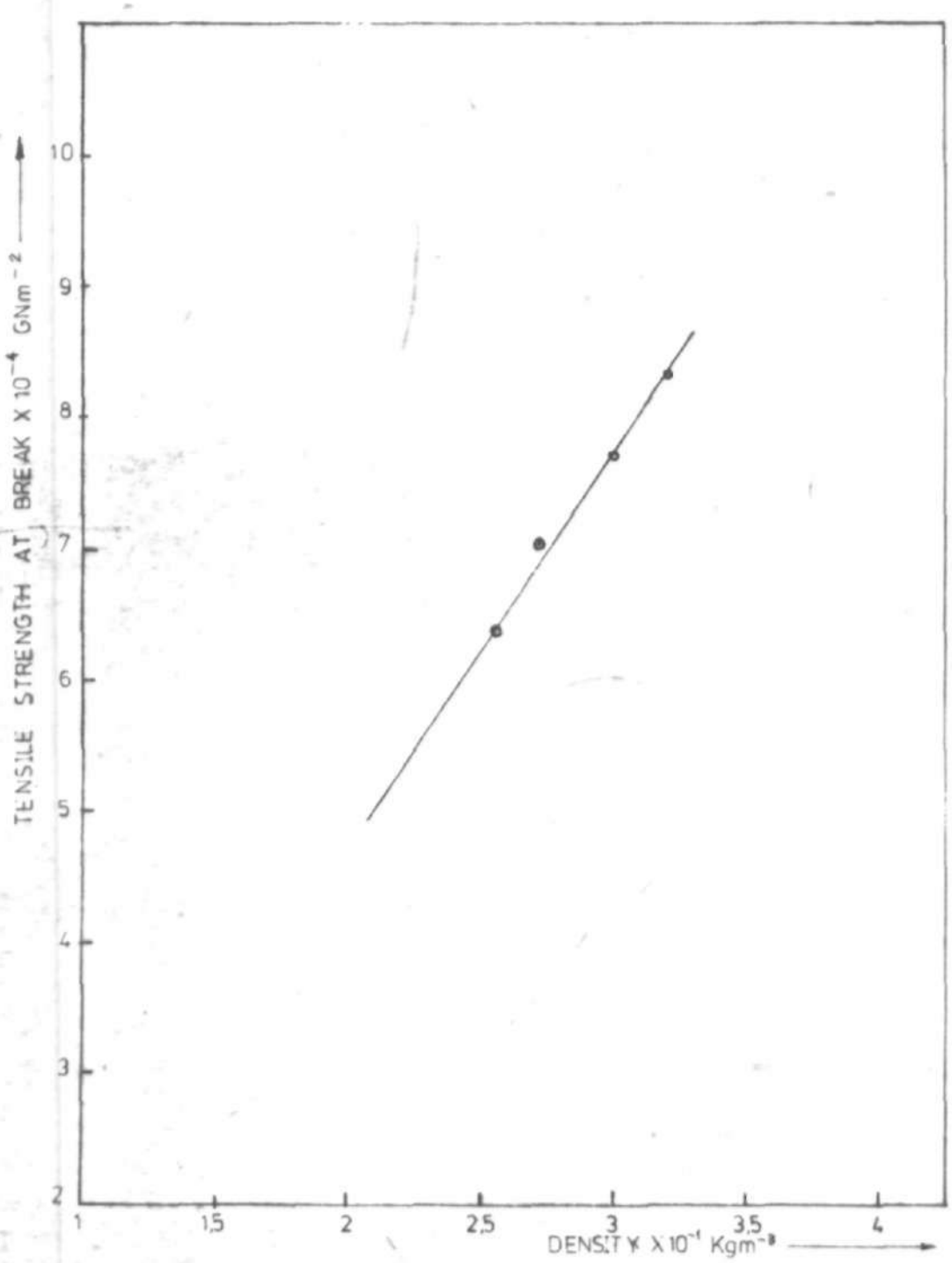


Fig 6 EFFECT OF DENSITY ON TENSILE STRENGTH AT THE BREAK OF FLEXIBLE POLYURETHANE FOAM

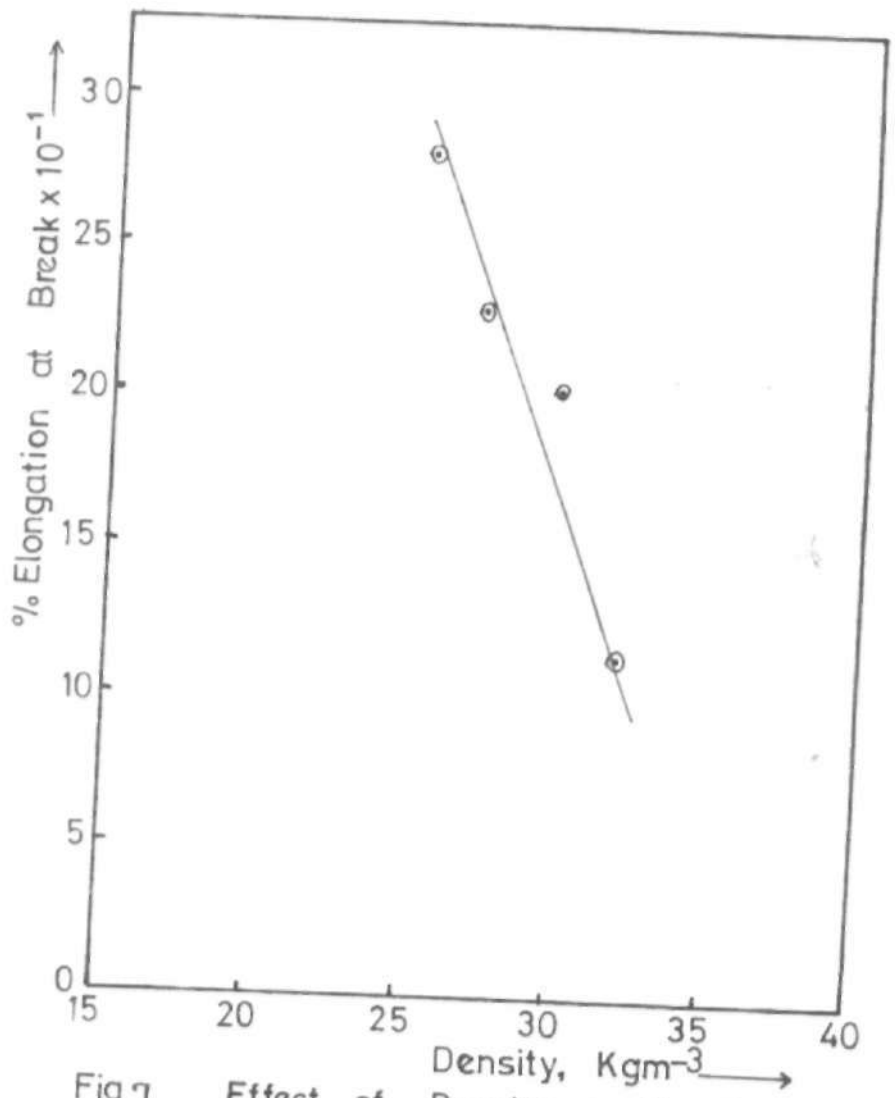


Fig 7 Effect of Density on % Elongation at Break of Flexible Polyurethane Foam $F_1 - F_4$

of larger density.

5.2 Control in the Rate of Evolution of Carbon dioxide

The results presented in Table 12 represent the average of three readings of the rise time values of flexible polyurethane foam preparation whose formulation included varying amounts of 1M sodium hydroxide solution.

In this investigation, the idea was to control the evolution of carbon dioxide by adding varying amounts of sodium hydroxide and thus determine the effect of this on the rate of evolution of carbon dioxide. The time for full rise of foams prepared by adding 0-4.70 cm^3 of 1M sodium hydroxide was recorded.

It can be seen (Table 12) that time rise fell from 115 seconds to 65 seconds when 0.50 cm^3 of 1M sodium hydroxide solution was added but with further addition of sodium hydroxide solution, rise time increased from 65 seconds to 142 seconds when 4.70 cm^3 of 1M sodium hydroxide solution was added. Visual examination of the foam prepared in this way did not indicate a significant increase in size of the foam on addition of

Table 12

Control of the rate of production of Carbon dioxide and hence its effect on rise time in flexible polyurethane foam preparation.

Composition of Ingredients: Polyol = 2.5 milimoles, water = 16.7 milimoles, TDI = 23.0 milimoles, Stannous Octoate = 0.07 milimoles, Dimethylethanolamine = 0.67 milimoles and Silicone Copolymer = 0.10g

1M NaOH

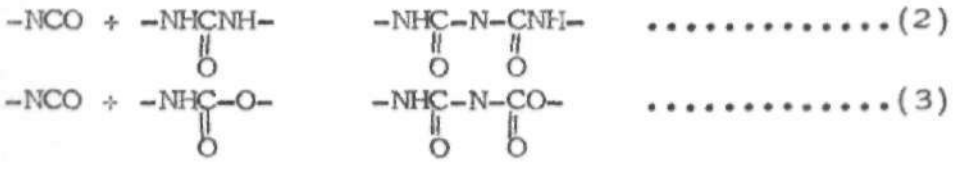
Volume of NaOH cm^3	Rise Time Secs.
0	115.0
0.50	65.0
1.20	76.5
2.30	97.5
4.70	142.5

sodium hydroxide solution. However, foams made in this way crumbled on touch (lost its strength) even on addition of trace amounts of sodium hydroxide solution and weaker bases such as sodium bicarbonate solution.

The earlier decrease in rise time is due to the additional water from added 0.50 cm^3 sodium hydroxide solution. This will increase the concentration of carbon dioxide and therefore the rate of evolution of carbon dioxide and probably responsible for the initial decrease in rise time. It appears the carbamic acid decomposition is retarded with increase in hydroxyl ion



concentration. The poor properties of these foams might have resulted from a premature gelation[30] of the foam as a result of the catalysation of the isocyanate urea reaction (31) to give a biuret and the isocyanate urethane reaction (32) to give an allophanate by the bases. Since these two equations are responsible for chain extension.



Premature gelations might also have been responsible for the increase in rise time.

5.3 Variation of mixed blowing agents concentration

Several workers have discussed the subject of blowing agents in polyurethane foam preparation but a definite information concerning the relationship between mixed blowing agents concentration in flexible polyurethane foam preparation and foam properties does not seem to be available. In this investigation therefore one is concerned with finding out the effect of using varying concentrations of more than one blowing agent at a time.

5.3.1 Density, Tensile stress and % Elongation of F_6-F_{13}

The effect of varying mixed blowing agents concentration in flexible polyurethane foam preparations on their properties is presented in Tables 13 and 14. Results illustrated in Figures 8 and 9 show the effect of freon content on density. It can be seen from these figures that probably because of the less cross-links in F_{10}-F_{13}, the density falls, more rapidly with increasing freon. The stress - strain curves are given

Table 13

Effect of mixed blowing agents on the physical properties of flexible polyurethane foams.

Composition of Ingredients: Polyol = 10.0g TDI = 23.0 milimoles, Stannous Octoate = 0.07 milimoles, Dimethylethanolamine = 0.67 milimoles and Silicone Copolymer = 0.10 g.

(a) Water = 16.7 milimoles

S/No of sample	Concentration of freon milimoles	Density Kgm^{-3}	Tensile Strength at break $\times 10^{-4}$ GNm^{-2}	% Elongation at break %E
F_1	0	32.14	8.31	114
F_6	1.16	31.60	8.21	119
F_7	2.32	27.90	7.62	224
F_8	4.64	25.40	6.84	248
F_9	9.28	22.30	6.48	260

(b) Water = 11.1 milimoles

S/No of	Concentration of Freon milimoles	Density Kgm^{-3}	Tensile Strength at break GNm^{-2}	% Elongation at break % E
F_0^1	0	41.16	-	-
F_{10}	1.16	40.02	13.70	184.0
F_{11}	2.32	37.50	11.10	187.0
F_{12}	4.64	32.00	9.70	192.5
F_{13}	9.28	25.50	7.25	196.7

Table 14

Stress - strain relationship for flexible polyurethane foams of varying proportions of mixed blowing agents concentrations.

(a) Water = 16.7 milimoles,

Freon = 1.16 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.27	5.5	0.49
100	0.50	10	0.97
150	0.72	14	1.46
200	0.93	18.5	1.94
250	1.15	23	2.43
300	1.35	27	2.91
350	1.60	32	3.40
400	1.90	38	3.89
450	2.25	45	4.37
500	2.65	53	4.86
550	3.15	63	5.34
600	3.75	75	5.83
650	4.40	88	6.31
700	5.20	104	6.80
750	6.15	123	7.28
800	7.20	144	7.77
845	8.40	169	8.21

(b) Water = 16.7 milimoles, Freon = 2.32 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.35	7	0.60
100	0.70	14	1.19
150	1.05	21	1.79
200	1.40	28	2.38
250	1.85	37	2.98
300	2.45	49	3.57
350	3.20	64	4.17
400	4.10	82	4.76
450	5.30	106	5.36
500	6.60	132	5.95
550	8.05	161.5	6.55
600	9.70	194	7.14
640	11.20	224	7.62

(c) Water = 16.7 milimoles, Freon = 4.64 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.35	14	0.43
100	0.60	24	0.85
150	0.80	32	1.28
200	0.95	38	1.71
250	1.15	46	2.13
300	1.35	54	2.56
350	1.60	64	2.98
400	1.90	76	3.41
450	2.20	88	3.84
500	2.60	104	4.26
550	3.05	122	4.69
600	3.55	142	5.12
650	4.20	168	5.54
700	4.80	192	5.97
750	5.50	220	6.40
760	6.20	248	6.82

(d) Water = 16.7 milimoles, Freon = 9.28 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.40	16	0.39
100	0.60	24	0.79
150	0.80	32	1.18
200	1.00	40	1.58
250	1.15	46	1.97
300	1.35	54	2.37
350	1.60	64	2.76
400	1.85	74	3.16
450	2.15	86	3.55
500	2.50	100	3.95
550	2.90	116	4.34
600	3.40	136	4.74
650	3.95	158	5.13
700	4.60	184	5.53
750	5.20	208	5.92
800	6.00	240.	6.32
820	6.50	260	6.48

(e) Water = 11.1 milimoles, Freon = 1.16 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.45	9	0.90
100	0.80	16	1.80
150	1.15	23	2.70
200	1.50	30	3.40
250	1.90	38	4.50
300	2.35	47	5.40
350	2.85	57	6.30
400	3.40	68	7.20
450	4.00	80	8.10
500	4.65	93	9.00
550	5.35	107	9.90
600	6.20	124	10.80
650	7.10	142	11.80
700	8.10	162	12.70
735	9.20	184	13.60

(f) Water = 11.1 milimoles, Freon = 2.32 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.70	14	1.10
100	1.35	27	2.20
150	2.05	41	3.30
200	2.70	54	4.40
250	3.30	66	5.50
300	4.20	84	6.60
350	5.30	106	7.70
400	6.50	130	8.80
450	7.90	158	10.00
500	9.08	181.5	11.00
504	9.35	187	11.10

(g) Water = 11.1 milimoles, Freon = 4.64 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.70	14	0.78
100	1.20	24	1.56
150	1.70	34	2.34
200	2.30	46	3.13
250	2.90	58	3.91
300	3.45	69	4.69
350	4.00	80	5.47
400	4.65	93	6.25
450	5.35	107	7.03
500	6.45	129	7.81
550	7.45	149	8.59
600	8.85	177.5	9.36
622	9.65	192.5	9.70

(h) Water = 11.1 milimoles, Freon = 9.28 milimoles

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.40	13.5	0.54
100	0.65	21.5	1.08
150	0.90	30	1.62
200	1.15	38.5	2.16
250	1.45	48.3	2.71
300	1.70	56.7	3.25
350	2.10	70	3.79
400	2.50	83.5	4.33
450	3.05	101.7	4.87
500	3.70	123.3	5.41
550	4.45	148.3	5.95
600	5.30	176.7	6.49
650	5.75	191.3	6.85
670	5.90	196.7	7.25

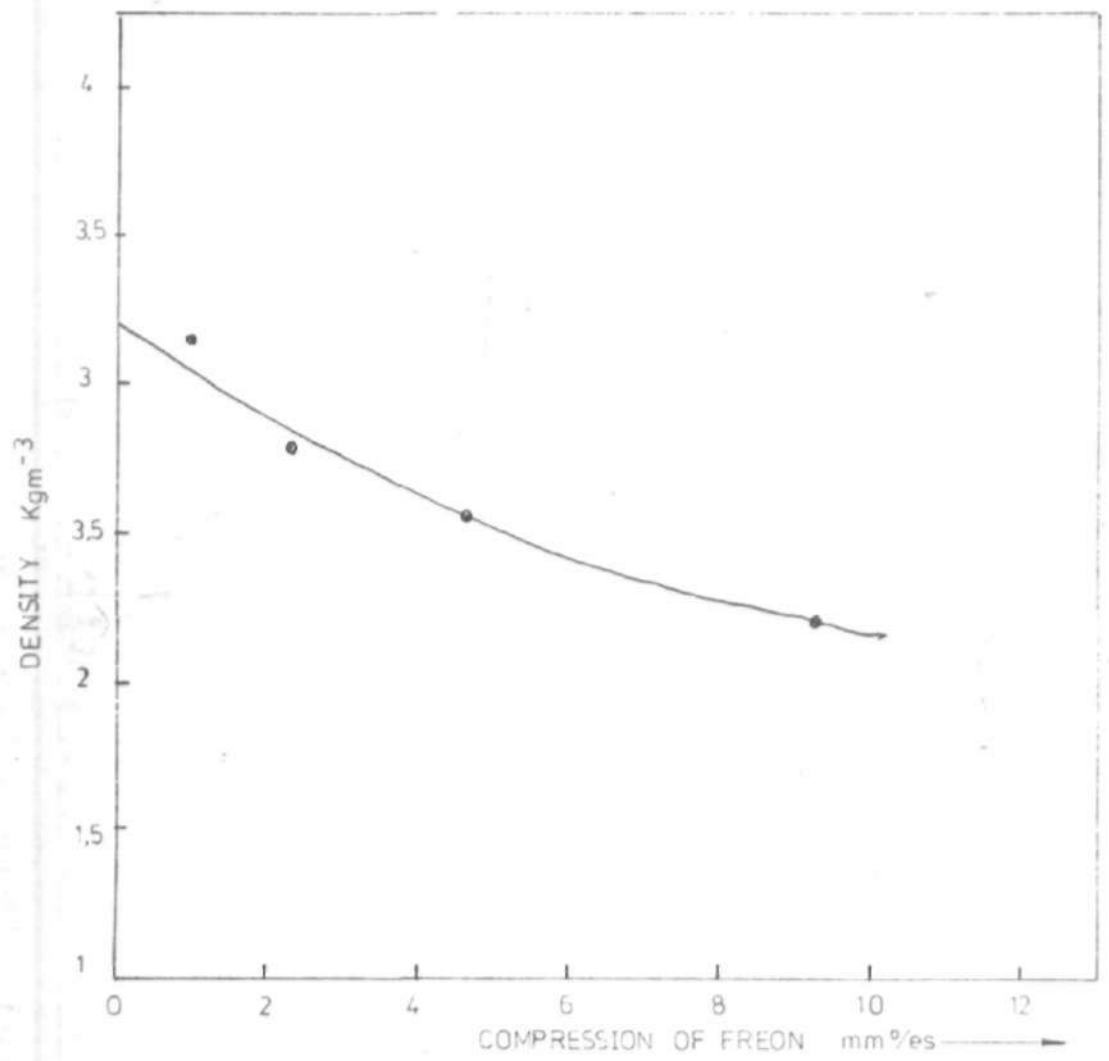


Fig.8 EFFECT OF FREON CONCENTRATION ON THE DENSITY OF FLEXIBLE POLYURETHANE FOAM

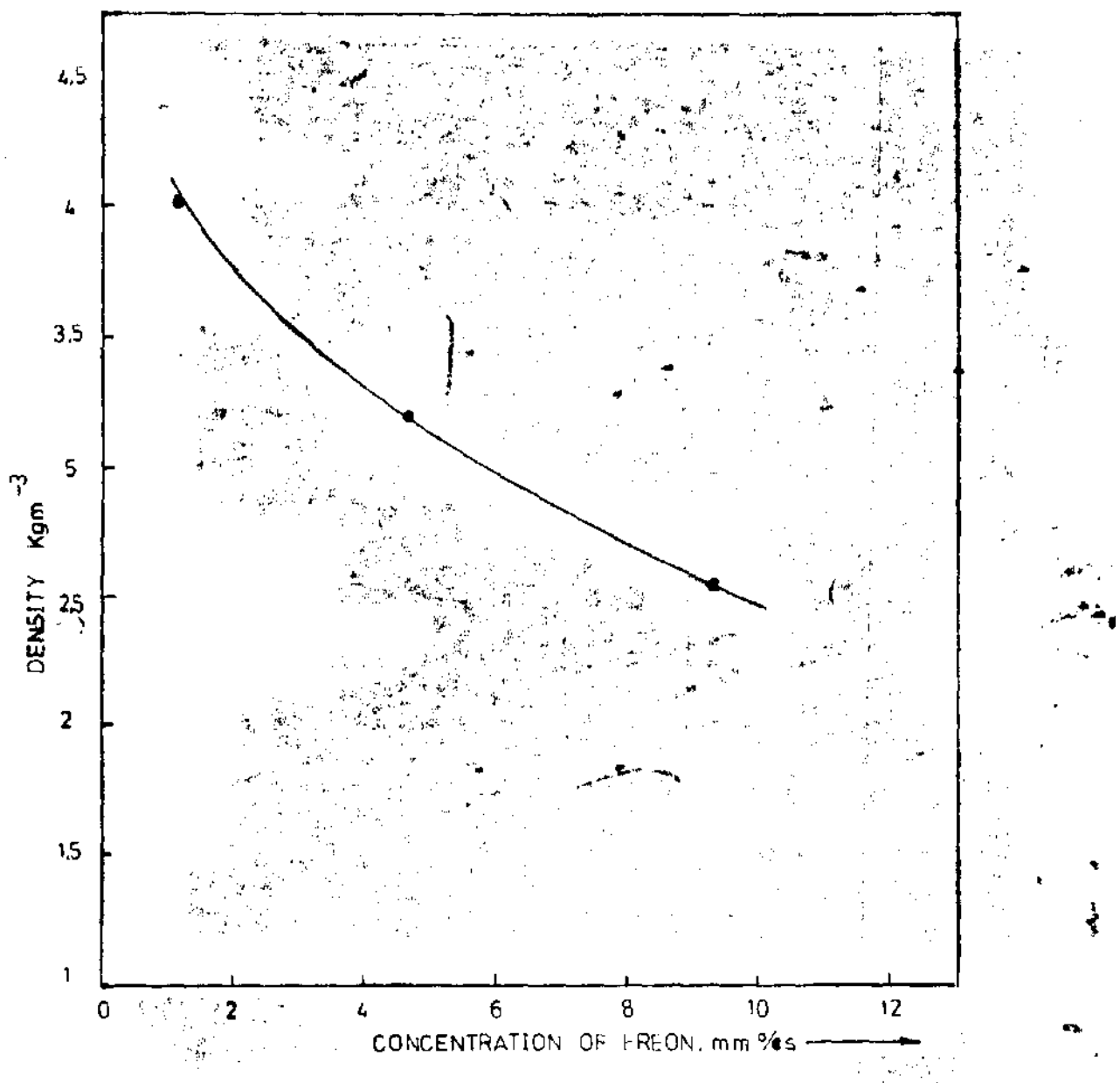


Fig 9 EFFECT OF FREON CONCENTRATION(WITH REDUCED AMOUNT OF WATER - 11,1mm%es) ON DENSITY OF FLEXIBLE POLY— URETHANE FOAM.

in Figure 10 and 11. The variation of tensile strength at break and % elongation at break with density are illustrated in Figures 12 and 13 respectively.

Figure 12 shows two groups of flexible polyurethane foams. One family represents a group containing 11.1 milimoles of water while the other contains 16.7 milimoles of water in their formulations. The family of foams containing 11.1 milimoles of water in their formulations have higher orders of physical properties than those containing 16.70 milimoles of water. This behaviour is probably due to the less cross-links contained in the former group (i.e. group containing 11.1 milimoles in their formulations) than for the later. Tensile strength at break falls with decrease in density and hence with increasing freon concentration. However for sample F_6-F_9 (See Figure 8) the decrease in density is faster than that for samples F_{10}-F_{13} (See Figure 9) with increase in freon content. % elongation at break for F_6-F_{13} again shows an inverse relationship to density. The % elongation at break for F_6-F_9 increases rapidly with decrease in density as shown in Figure 13 and tends to level up with further decrease in density. For samples F_{10}-F_{13} which have lower amount of water

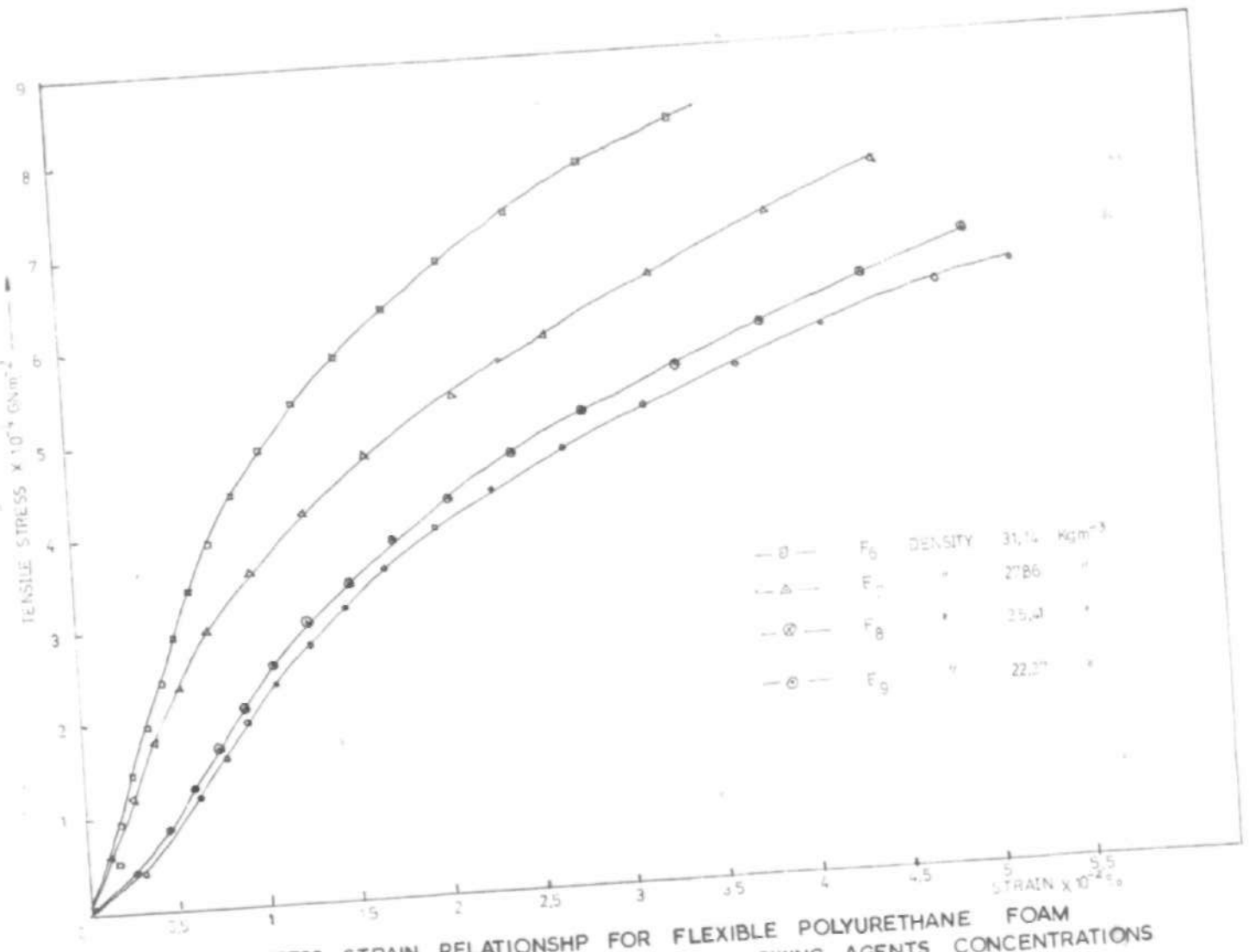


FIG 10 STRESS-STRAIN RELATIONSHP FOR FLEXIBLE POLYURETHANE FOAM OF VARYING PROPORTIONS IF MIXED BLOWING AGENTS CONCENTRATIONS

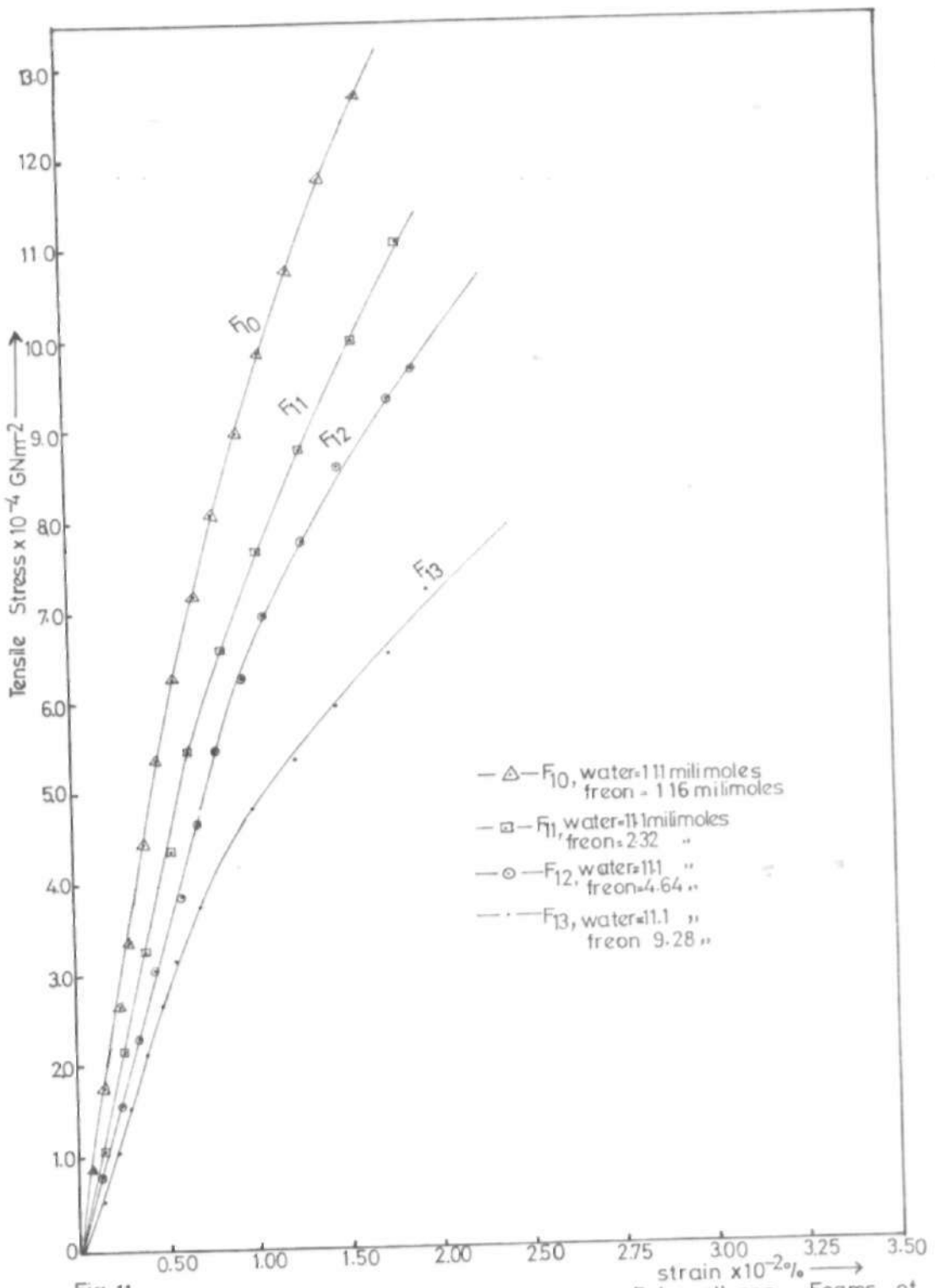


Fig 11 Stress-Strain Relationship for Flexible Polyurethane Foams of Varying Proportions of Mixed Blowing Agents

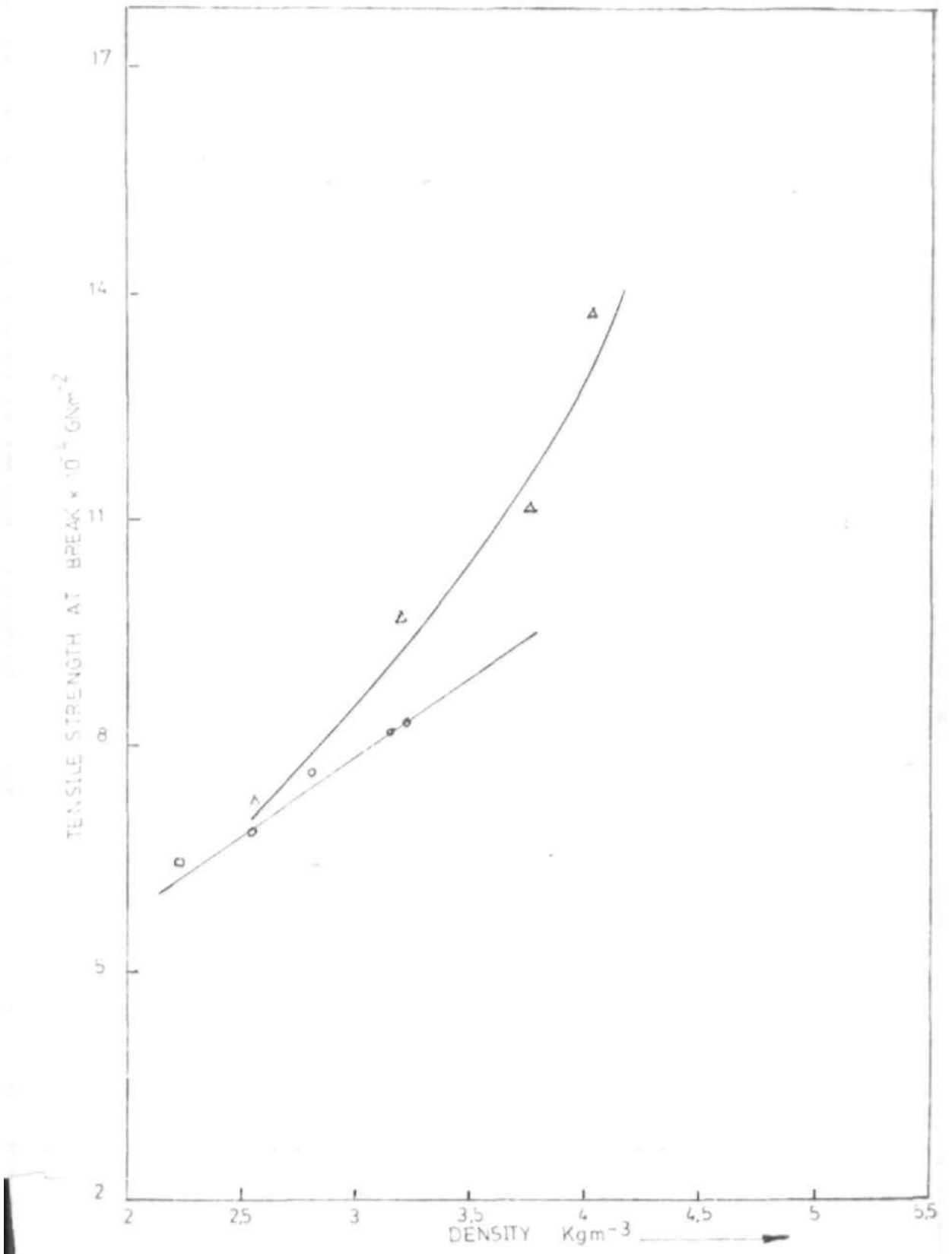


Fig12 EFFECT OF DENSITY ON TENSILE STRENGTH AT BREACK FOR Fi (i= 6, 7---13)

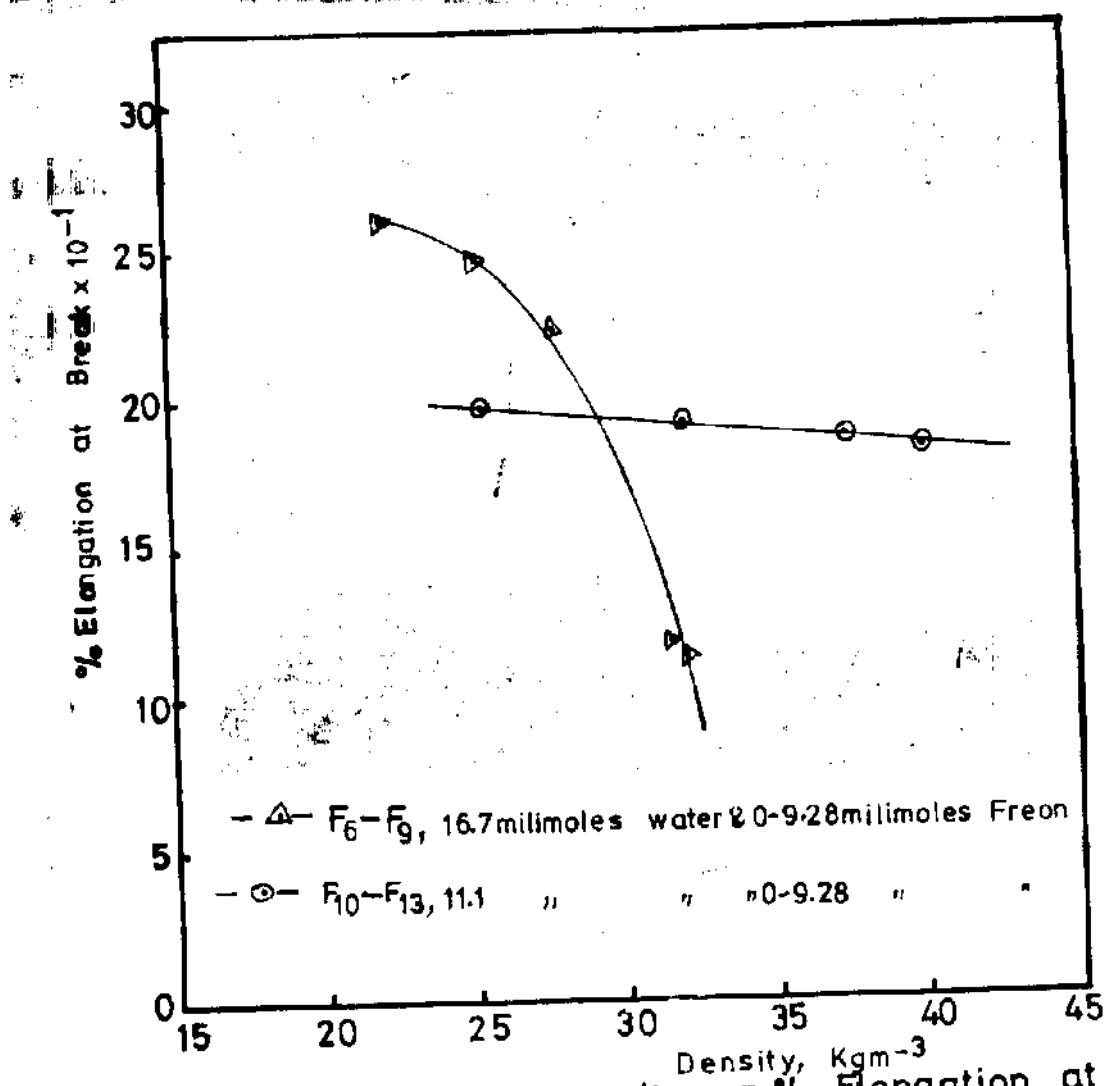


Fig 13 Effect of Density on % Elongation at Break of Flexible Polyurethane Foam F_6 — F_{13}

in their formulation, the increase in % elongation with decrease in density is much slower than for samples F_6-F_9.

Comparison of the curves in Figures 12 and 13 show that the foams with lower water content in their formulations show faster decrease in tensile strength and slower increase in % elongation with decrease in density (i.e. with increasing freon content). The reverse is the case with the foams with higher water content. This again can be explained by saying that the family of foams with greater crosslinks would have a greater elongation per unit load than the family with smaller crosslinks. The increasing elongation with decreasing density and hence increasing freon content is due to the fact that a given load would be expected to produce a greater elongation in a material of lower density than one of greater density.

It does appear from the comparisons of F_6-F_9 and F_{10}-F_{13} that it is not wise to solely relate density to all other physical properties, rather properties can also be varied by playing with the blowing agents in flexible polyurethane foam formulations.

5.4 Effect of rise height on properties of flexible polyurethane foams

The effect of rise height on the physical properties of flexible polyurethane foams is presented in Tables 15 and 16 and illustrated in Figures 14, 15 and 16.

Results presented in Table 15 indicate that rise height has a very significant effect on density, particularly at a height rise of about less than 6.00 cm. This fact is illustrated in Fig.14 where the density has been shown to gradually increase with decrease in rise height and later increases eratically.

The observed trend can be explained by recalling that the size of a bubble of gas coming off from the bottom of a container containing a liquid increases in size towards the surface. There is no doubt therefore that the sizes of these bubbles some of which are trapped in the foam are bound to affect foam properties. The exact manner by which these bubbles affect foam strength is not very clear but it can be said that they perhaps disrupt urethane linkages and also prevent close

Table 15

Effect of Rise height on the physical properties of flexible polyurethane foams.

Composition of Ingredients: Polyol = milimoles Water = 33.3 milimoles, TDI = 46.0 milimoles, Stannous Octoate = 0.14 milimoles, Dimethylethanolamine = 1.34 milimoles and Silicone Copolymer = 0.20 g.

S/No of sample	Rise height cm	Density Kgm^{-3}	Tensile Strength at break x 10^{-4} GNm^{-2}	% Elongation at break %E
F_{14}	3.80	67.54	22.84	222.5
F_{15}	6.00	59.03	21.70	225.0
F_{16}	7.10	53.11	15.29	231.0
F_{17}	8.40	52.54	14.60	247.5

Table 16

(

Stress - Strain relationship for flexible polyurethane foams of varying rise heights.

Rise height = 3.80 cm

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.50	10	1.52
100	1.00	20	3.05
150	1.40	28	4.57
200	1.80	36	6.09
250	2.25	45	7.61
300	2.70	54	9.14
350	3.25	65	10.66
400	3.85	77	12.18
450	4.60	92	13.71
500	5.45	109	15.23
550	6.50	130	16.75
600	7.55	151	18.27
650	8.00	176	19.80
700	9.75	195	21.32
750	11.15	222.5	22.84

Rise height = 6.00 cm

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.75	15	1.53
100	1.35	27	3.06
150	1.80	36	4.59
200	2.20	44	6.13
250	2.60	52	7.66
300	3.05	61	9.19
350	3.65	73	10.72
400	4.30	86	12.25
450	5.00	100	13.78
500	5.85	117	15.31
550	6.80	136	16.85
600	7.90	158	18.38
650	9.40	188	19.85
700	11.05	221.5	21.42
709	11.25	225.0	21.70

Rise height = 7.10 cm

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.60	12	0.80
100	1.00	20	1.61
150	1.35	27	2.41
200	1.65	33	3.22
250	2.00	40	4.02
300	2.25	45	4.83
350	2.55	51	5.63
400	2.90	58	6.44
450	3.30	66	7.24
500	3.75	75	8.05
550	4.25	85	8.85
600	4.80	96	9.65
650	5.45	109	10.46
700	6.15	123	11.26
750	6.95	139	12.07
800	7.80	156	12.87
850	8.90	178	13.68
900	10.05	201	14.48
950	11.55	231	15.29

Rise height = 8.40 cm

Load gm	Extension cm	% Strain %E	Stress x 10^{-4} GNm^{-2}
50	0.60	15	0.85
100	1.03	26	1.70
150	1.43	36	2.56
200	1.80	45	3.41
250	2.10	52.5	4.26
300	2.40	60	5.11
350	2.68	67	5.97
400	3.00	75	6.82
450	3.35	84	7.67
500	3.80	95	8.52
550	4.25	107.5	9.38
600	4.80	120	10.23
650	5.45	137.5	11.08
700	6.15	155	11.93
750	6.90	172.5	12.79
800	8.00	200	13.64
850	9.50	237.5	14.49
856	9.90	247.5	14.60

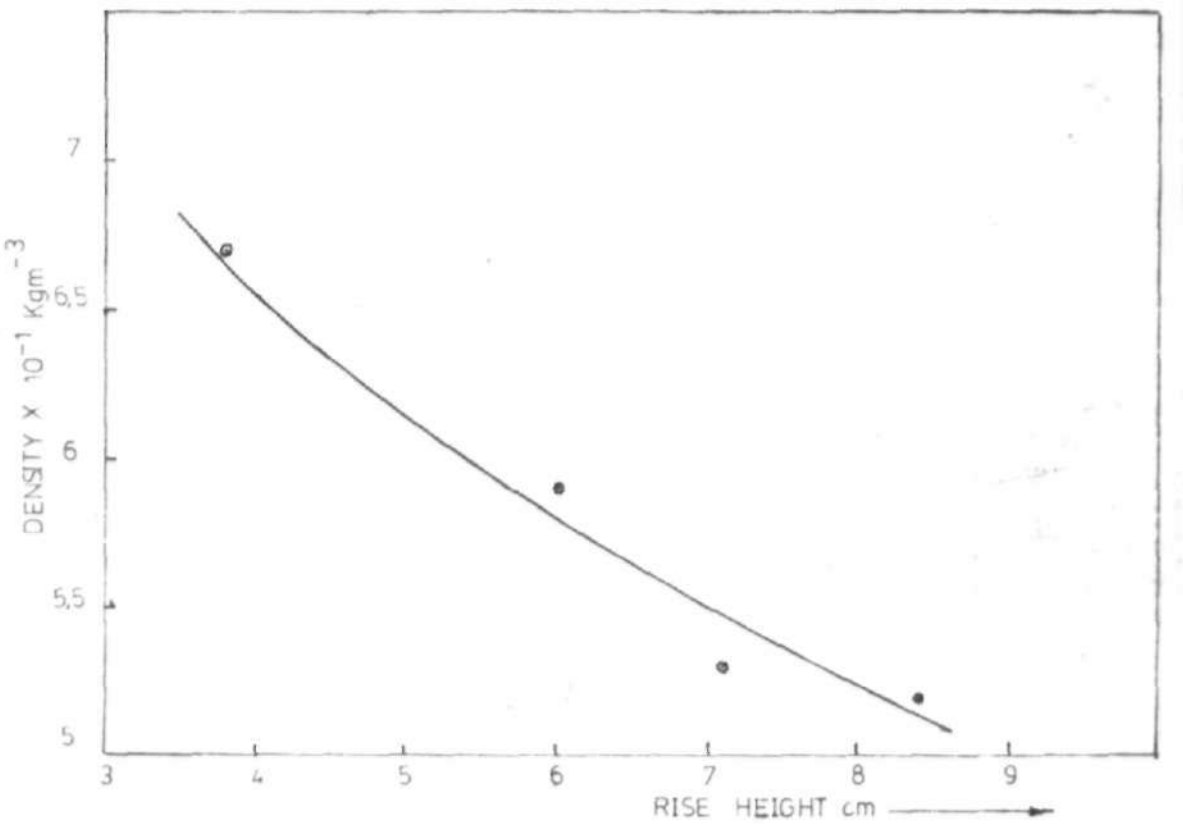


Fig 14 EFFECT OF RISE HEIGHT ON DENSITY OF FLEXIBLE POLYURETHANE FOAM

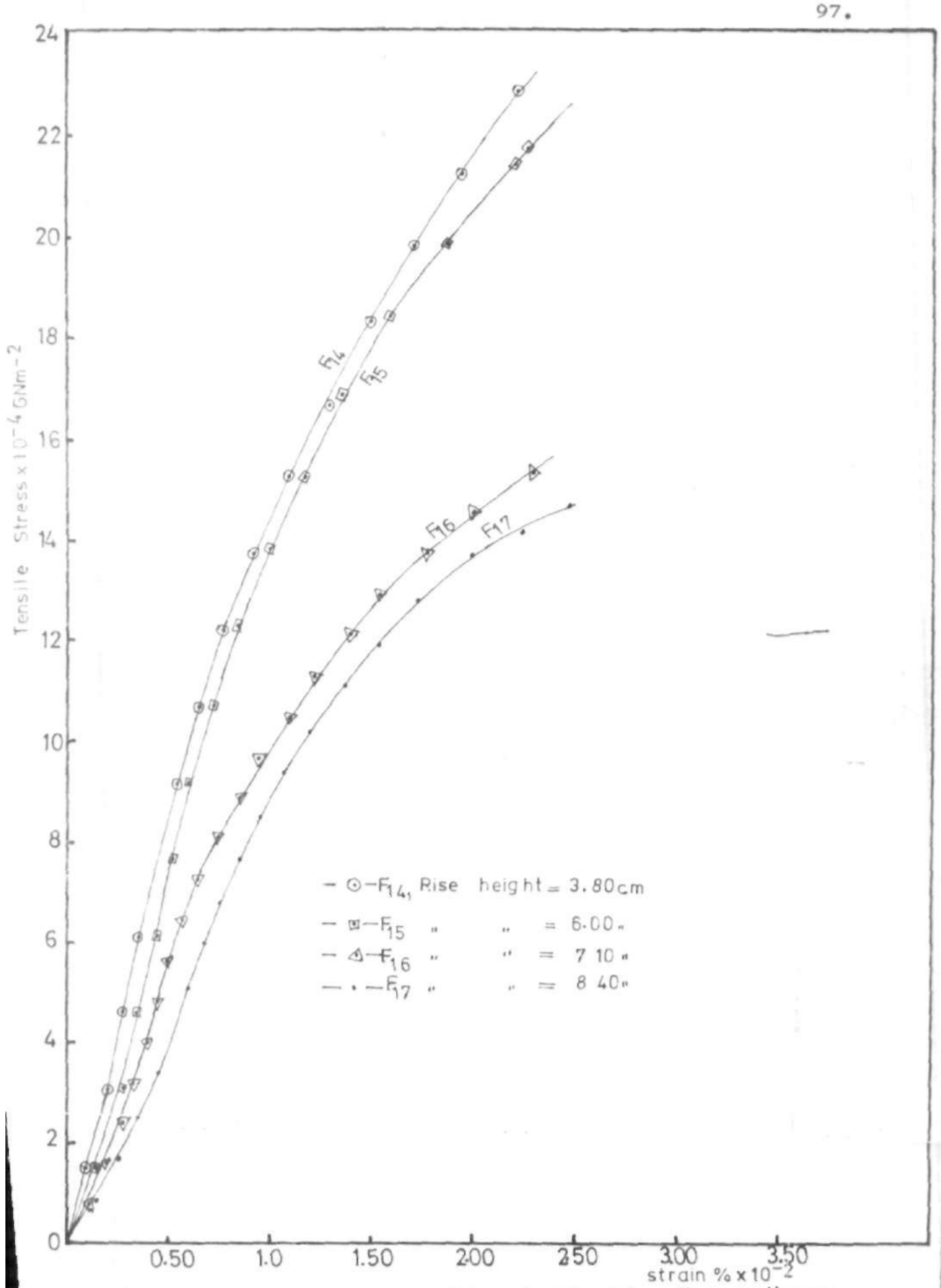


Fig 15 Stress Strain Relationship of Flexible Polyurethane Foams of Varying Rise Heights

structures because of their larger size at large rise height. A visual observation of F_{14} showed that the upper part of the foam was very hard and smooth which lends some credibility to the explanation offered above. Fig 15 again shows that the initial modulus decreases with rise height. Fig. 16 shows a graphical representation of Tensile strength variation of foams F_{14}, F_{15}, F_{16} and F_{17} with density and hence rise height. The tensile strength again depend largely on the density and hence rise height.

Though a drastic decrease in rise height will not be of commercial interest because of the small size of foam formed. Nevertheless, these studies in the control of foam height in a continuous manufacturing process is relevant. It is therefore of utmost importance to control the rise height to get products of acceptable properties. In the continuous manufacturing process, the foams are made in a slab form. The speed of the conveyor belt controls the cross-sectional area and thus equivalent to the cross-sectional area of the wooden moulds in this investigation. The blended

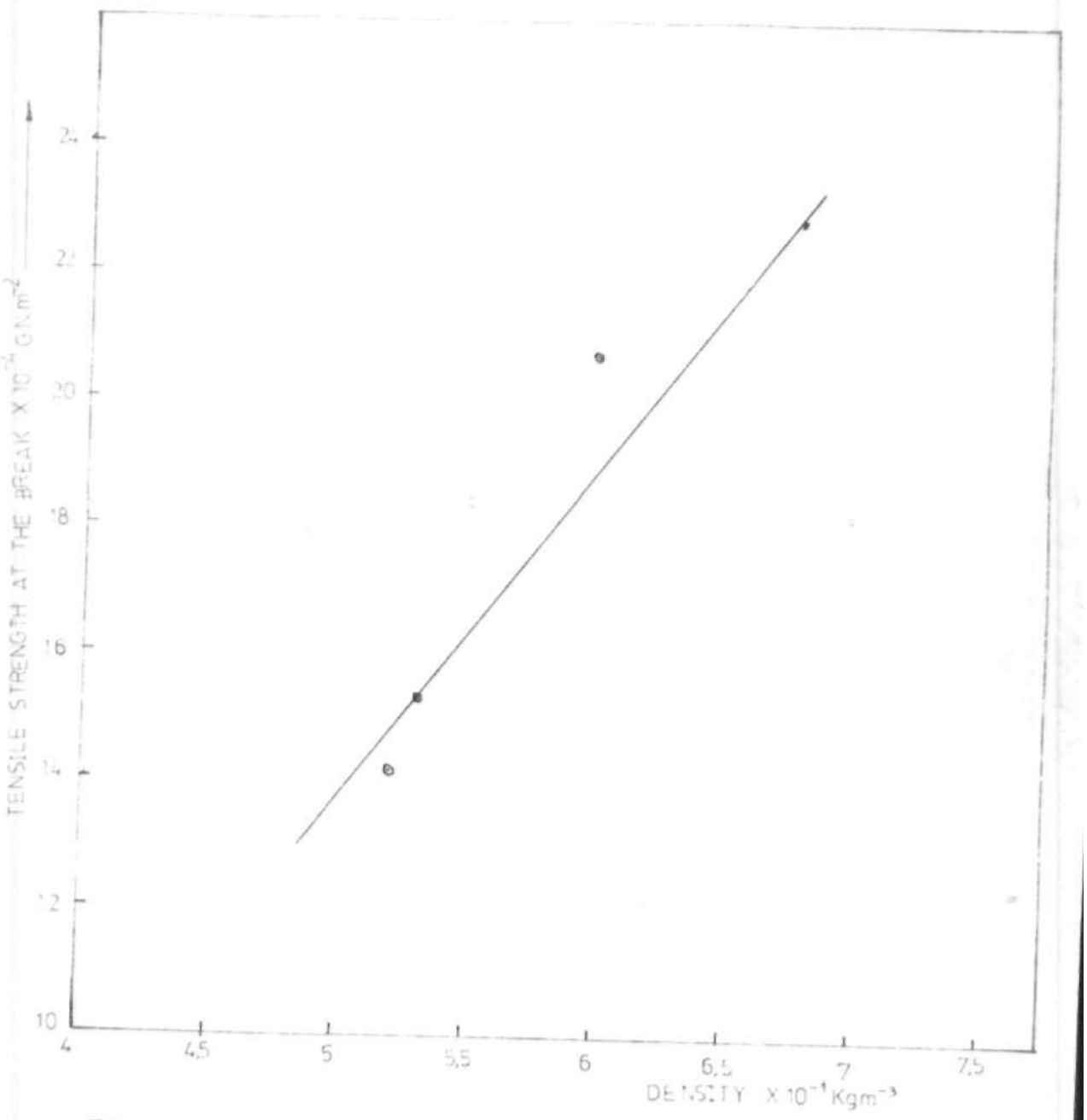


Fig16 EFFECT OF DENSITY ON THE TENSILE STRENGTH AT BREAK OF F_{14}, F_{15} F_{16} AND F_{17}.

reactants are delivered onto a slab a fixed discharge rate and the conveyor belt controls the rise height of the polyurethane foam slab.

5.5 Compression stress-strain behaviour

5.5.1 Flexible polyurethane foam

Flexible polyurethane foams are widely used in comfort cushioning among other uses. One of the properties of greatest significance in cushioning applications of cellular polymers is compression behaviour.

Figure 17 illustrates the comprehensive behaviour of flexible polyurethane foams F_{10}-F_{13} prepared by fixing amount of water at 11.1 milimoles while keeping the concentration of all the other ingredients constant and varying freon content between 0-9.28 milimoles. The strain (i.e. % compression) corresponding to various stresses is shown in Table 17. It can be deduced from Figure 17 that the load-compression curves of flexible polyurethane foam samples show pronounced s-shaped behaviour and also display some permanent set (for first cycle deformation). The consequence of the s-shaped curves is that the materials display sharp yield points.

Table 17

Load-Compression relationship of flexible polyurethane foams of varying densities under a compressive stress.

F_{10}, density = 40.02 kgm^{-3}, F_{11}, density = 37.5 kgm^{-3};
F_{12}, density = 32.00 kgm^{-3}, F_{13}, density = 25.5 kgm^{-3}

Load x 10^{-1} (kg)				Compression %			
F_{10}	F_{11}	F_{12}	F_{13}	F_{10}	F_{11}	F_{12}	F_{13}
0.68	0.45	0.30	0.15	5.1	5.6	5.6	5.6
0.82	0.45	0.30	0.15	10.2	11.1	11.1	11.1
0.82	0.45	0.30	0.15	15.3	16.7	16.7	16.7
0.82	0.45	0.30	0.15	20.4	22.2	22.2	22.2
0.90	0.45	0.30	0.15	25.5	27.8	27.8	27.8
0.90	0.45	0.30	0.15	30.6	33.3	33.3	33.3
1.01	0.45	0.30	0.23	35.7	38.9	38.9	38.9
1.01	0.52	0.37	0.30	40.8	44.5	44.4	44.5
1.05	0.60	0.45	0.34	45.9	50.0	50.0	50.0
1.13	0.65	0.50	0.34	51.0	55.6	55.6	55.6
1.20	0.75	0.54	0.38	56.1	61.1	61.1	61.1
1.43	0.94	0.68	0.38	61.2	66.3	66.2	66.3
1.76	1.27	0.86	0.41	66.3	72.2	72.2	72.2
3.00	2.17	1.12	0.49	71.4	77.8	77.8	77.8
5.25	4.73	1.55	0.60	76.5	83.3	83.3	83.3
6.62	9.15	3.60	0.94	77.8	88.9	88.9	88.9
9.98	-	5.99	2.78	81.6	9	91.7	94.5
-	-	8.75	8.55	-	-	94.4	99.5

The samples feel hard until some 6-10% compression has been achieved, whereupon a pronounced softening occurs, with a large compression strain occurring for very little additional load, until a stage of about 40% compression is reached where an ultimate stiffening occurs. A. Barnatt[2] explained the practical application of this property by saying that impacts are absorbed by the flexible foam, which recover their original shape after the source of impact has been removed.

5.5.1.1 Yield Index and Step Factor

The unfortunate usage of the term modulus as stress at a prescribed strain in Load - compression studies of polyurethane foams has its origin in the non-linearity of the stress-strain curves of the materials. The compression modulus of a sample of foam is therefore equal to the compressive stress which is required to produce a specified compression strain. A further anomally is that stresses (whether compressive or tensile) are usually refered to the initially cross-sectional area of the unstrained test piece. Thus load and stress have precisely the same significance, although they differ by a numerical factor which represents the initial

cross-sectional area of the test piece.

The modulus for samples F_{10}-F_{13} at various strains are given in Table 17.

Because of the non-linearity of the curves, various workers have suggested the use of one parameter for satisfactory comparison. Thus Carey and Rogers defined a yield index as the ratio of the load required to produce 50% compression to that required to produce 10% compression while Packer and Wood proposed a step factor which they defined as 2 minus the ratio of the stress required to produce 40% compression to that required for 20% compression. The step factor values for F_{10}-F_{13} are more or less constant and did not appear to be useful in characterising the foams studied. Table 18 shows that yield indices of the foams studied. There appears to be an increase in yield index with increase in blowing agent concentration and hence decrease in density. The results shown in Table 18 also seem to show that foams with high yield indices are more comfortable than those with low yield indices since the load needed for initial deformation is low thus providing

comfort while the higher load at 50% compression provides the necessary firmness for support.

5.5.1.2 Hysteresis

The compression stresses corresponding to strains in the forward and backward directions were calculated from the results obtained. These values obtained are shown in Table 19 while Figures 18 and 19 illustrate the hysteresis behaviour of flexible foam. The low hysteresis compared to R_1-R_4 (See section 5.4.2.2) means that not much energy is absorbed during cyclic deformation, and that the resilience is therefore comparatively high.

5.5.2 Rigid polyurethane foam

For rigid foams, no tensile properties were studied as they showed very poor tensile properties. Rigid foams are used for thermal insulation purposes and in furniture. In these uses, they are subjected to compressive stresses. Hence the significance of studies in compressive behaviour. Table 20 shows the effect of freon content on density of rigid foams.

Table 18

Yield Indices and step factors of F_{10}-F_{13}

S/No of sample	Density Kgm^{-3}	Load ($Kg\ 19cm^2$) at 10%	20%	40%	50%	Yield Index	Step Factor
F_{10}	40.02	81.0	81.0	96.8	109.4	1.35	0.81
F_{11}	37.50	45.0	45.0	47.3	64.4	1.43	0.95
F_{12}	32.00	28.8	27.0	27.0	44.1	1.56	1.00
F_{13}	25.50	15.3	15.8	17.1	29.3	1.71	0.91

Table 19

Hysteresis loss of flexible polyurethane foams F_{10}-F_{13}.
F_{10}, density = 40.02 kgm^{-3}; F_{11} density = 37.5 kgm^{-3}
F_{12}, density = 32.00 kgm^{-3}; F_{13} density = 25.5 kgm^{-3}

Load x 10^{-1} ($Kg\ 19\ cm^2$)				Compression %			
F_{10}	F_{11}	F_{12}	F_{13}	F_{10}	F_{11}	F_{12}	F_{13}
9.97	9.14	8.75	8.55	81.3	89.0	94.3	98.0
5.25	5.25	6.84	5.09	85.2	86.7	97.2	98.0
2.70	3.00	4.56	2.25	83.2	85.6	96.0	97.0
0.75	0.75	0.75	0.30	76.5	82.8	94.5	95.8

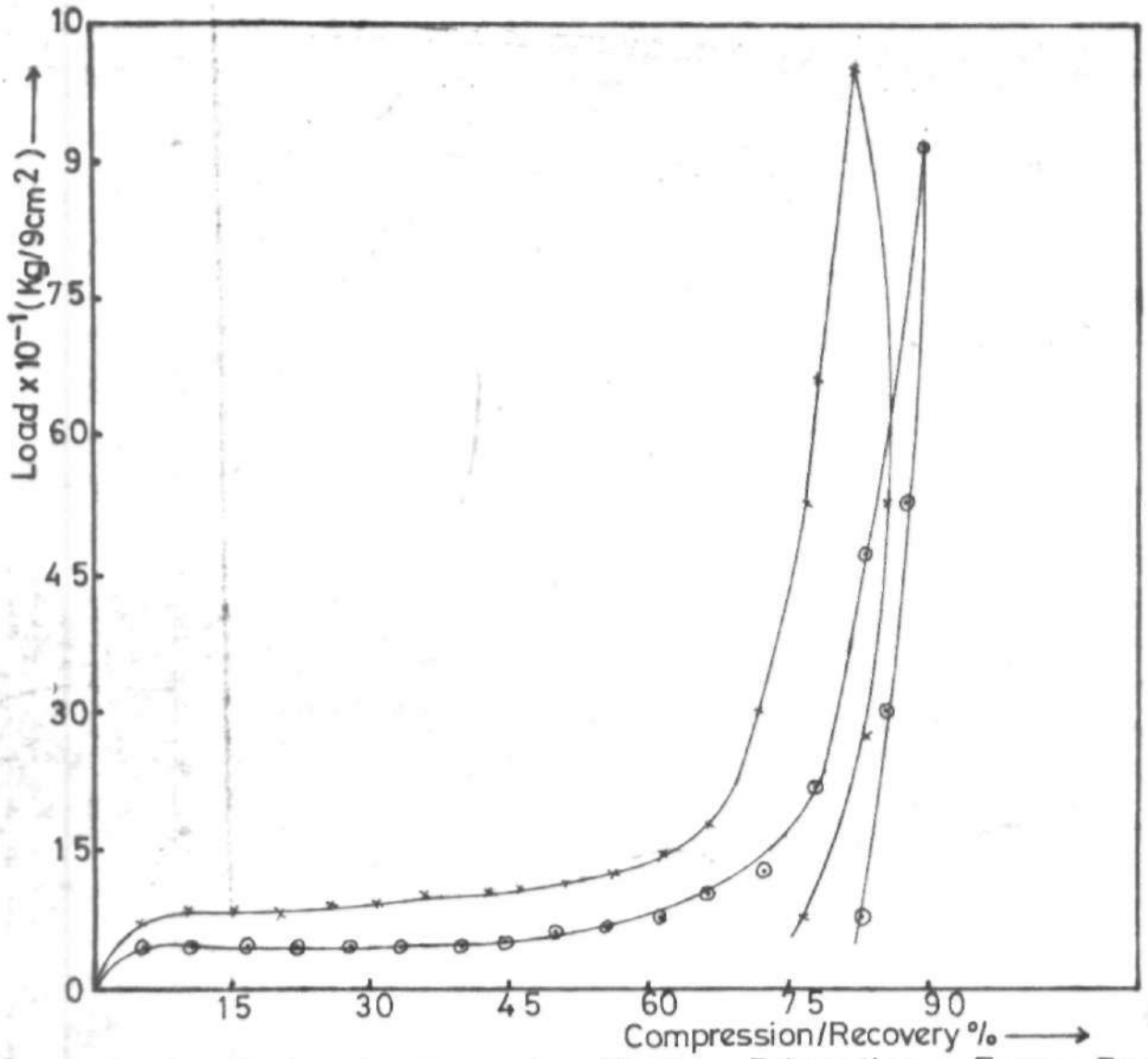


Fig 18 Hysteresis Loss for Flexible Polyurethane Foams $\bar{r}_{11}$ & $\bar{r}_{m}$

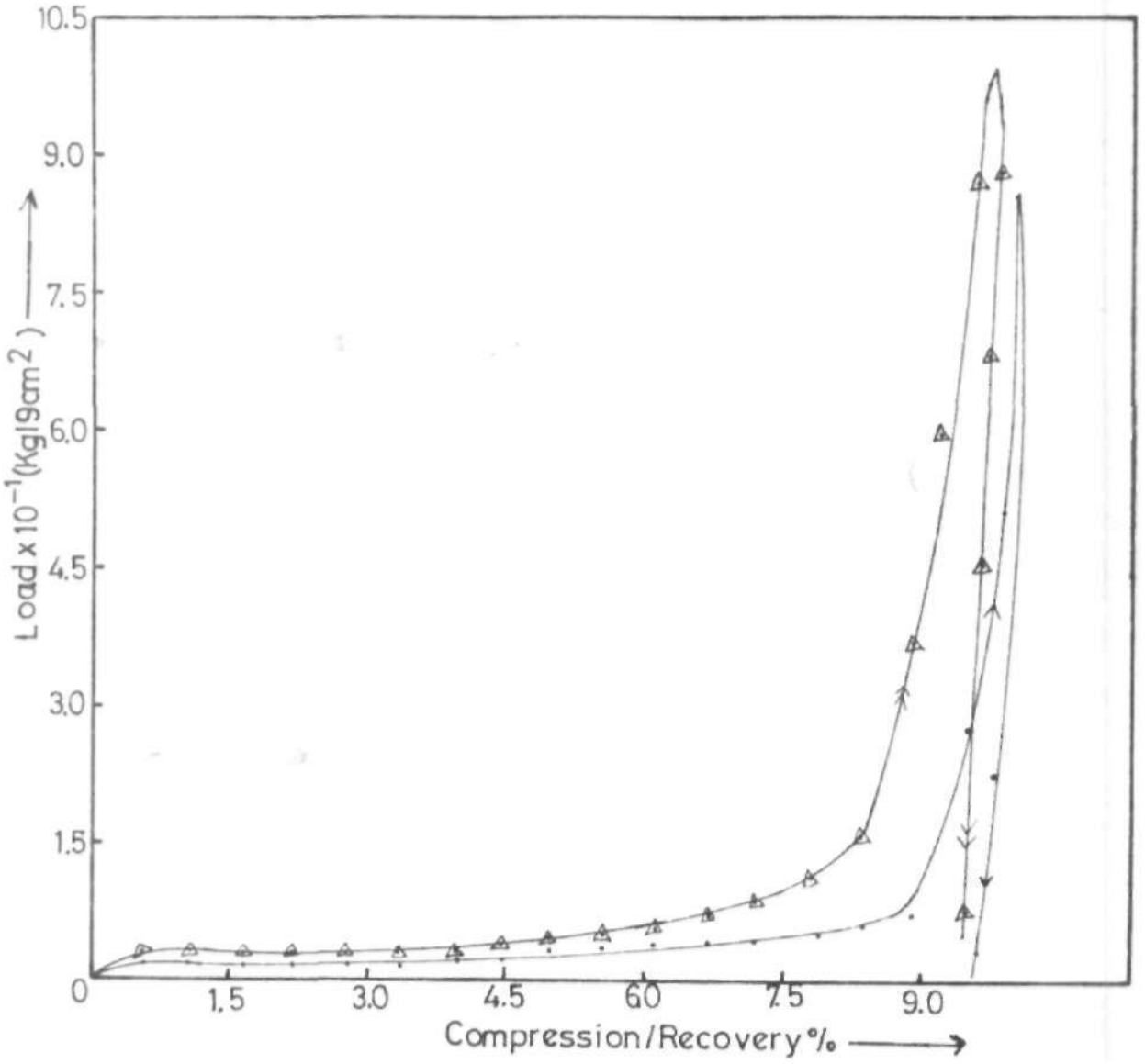


Fig 14 Hysteresis Loss for Flexible Polyurethane Foams f_{12} & f_{13}

Table 20

Effect of freon concentration on density of rigid polyurethane foams.

Composition of ingredients: Polyol and appropriate proportions of catalyst, stabiliser, fire retardant = 10g and 4,4' di-isocyanate-diphenylmethane (MDI) = 3.5g

S/No. of sample	Freon Concentration milimoles	Density Kgm^{-3}
R_1	1.16	34.59
R_2	2.32	33.80
R_3	4.64	30.58
R_4	9.28	23.06

The compressive stress and corresponding modulus were calculated for R_1-R_4. These are shown in Table 21 and illustrated in Figure 20.

It can be seen from Figure 20 that the curves here again are s-shaped as is the case for flexible foams - but not a sharp point of inflection. This implies that the yield points are not as precise as for flexible foams. The samples feel hard until some 6-10% compression has been reached but the modulus required to produce this strain is much greater than for flexible foams (compare Tables 17 and 21). Softening is not very pronounced in rigid foams as was the case for flexible foams. Ultimate stiffening occurs after a much greater strain (about 60-70%) as compared to about 40% in flexible foams.

5.5.2.1 Yield Index

The method of Carey and Rogers was again employed in calculating the yield indices of R_1,R_2,R_3 and R_4. The calculated values are given in Table 22. A comparison of F_{13} (density =25.50 kgm^{-3}) and R_4(density = 23.06kgm^{-3}) shows that the former has a higher yield index than the later even though its density is still considerably

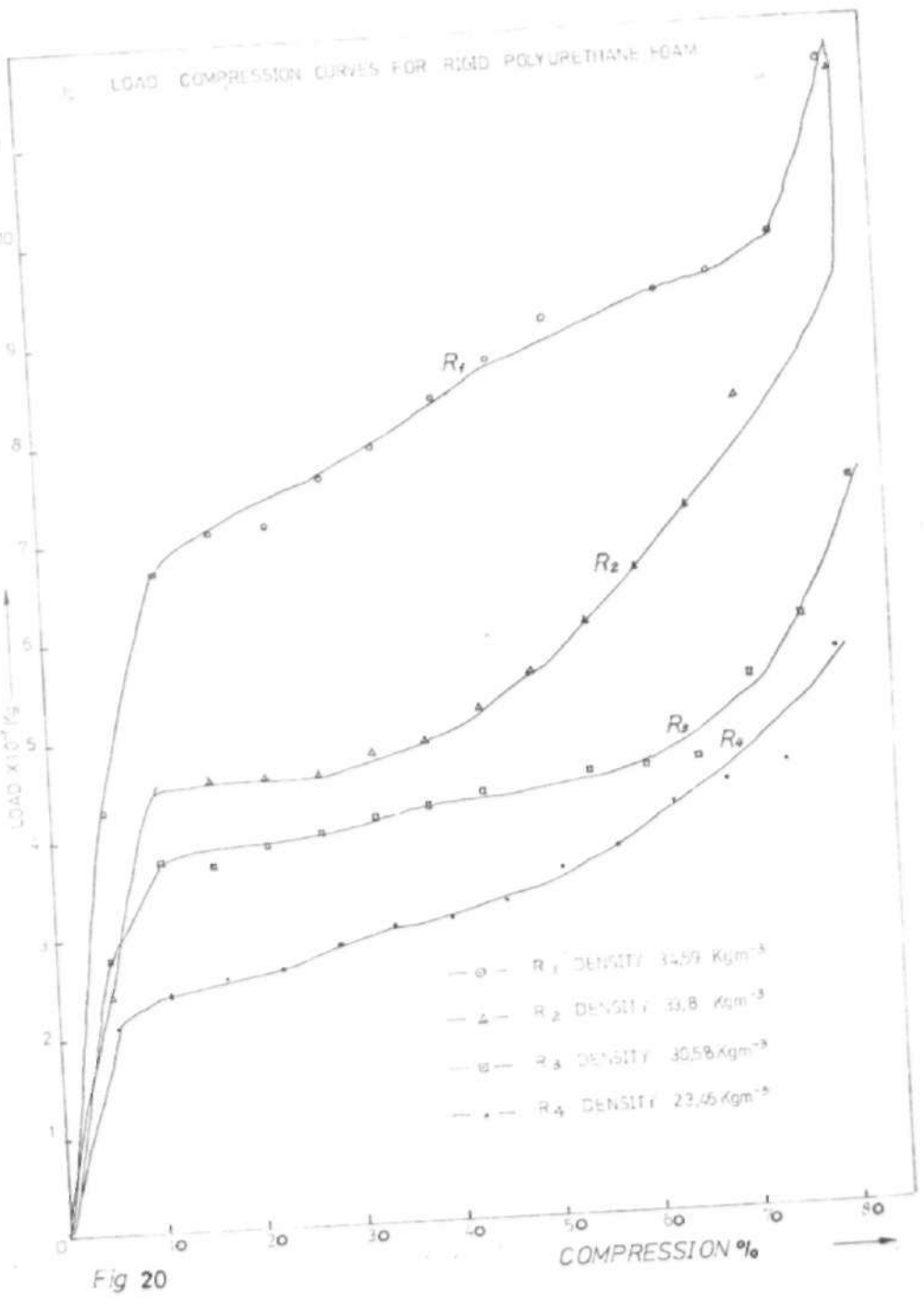

LOAD COMPRESSION CURVES FOR RIGID POLYURETHANE FOAM
LOAD KG
COMPRESSION %
R1
R2
R3
R4
— ⊙ — R1 DENSITY 34.59 Kgm-3
— △ — R2 DENSITY 33.8 Kgm-3
— ⊡ — R3 DENSITY 30.58 Kgm-3
— • — R4 DENSITY 23.46 Kgm-3

Fig 20

Table 21

Load-Compression relationship of rigid polyurethane foams of varying densities under a compressive stress.

R_1, density = 34.59 kgm^{-3}; R_2, density = 33.80 kgm^{-3}

R_3, density = 30.58 kgm^{-3}; R_4, density = 23.06 kgm^{-3}

Load x 10^{-1} ($Kg/9cm^2$)				Compression %			
R_1	R_2	R_3	R_4	R_1	R_2	R_3	R_4
4.28	2.40	2.78	2.10	5.8	5.4	5.4	5.7
6.67	4.50	3.75	2.40	11.5	10.9	10.9	11.4
7.05	4.58	3.67	2.55	17.2	16.3	16.3	17.1
7.09	4.58	3.86	2.62	23.0	21.7	21.7	22.7
7.57	4.58	3.97	2.85	28.8	27.2	27.2	28.4
7.88	4.78	4.09	3.00	34.5	32.6	32.6	34.1
8.33	4.87	4.20	3.07	40.2	38.0	38.0	39.8
8.70	5.21	4.33	3.19	46.0	43.5	43.5	45.5
9.08	5.55	4.20	3.52	51.7	48.9	48.9	51.1
8.92	6.00	4.46	3.83	57.5	54.4	54.4	56.8
9.30	6.53	4.50	4.15	63.2	59.8	59.8	62.5
9.45	7 .12	4.58	4.35	68.4	65.2	65.2	68.1
9.82	8.21	5.40	4.50	74.7	70.7	70.70	73.9
11.55	9.37	6.93	5.62	80.5	76.1	76.1	79.6
-	11.47	7.34	-	-	81.5	81.5	-

greater. Following the earlier deductions, it is obvious that rigid foams are not good for comfort cushioning.

5.5.2.2 Hysteresis

The compression stress-strain in the forward and backward directions were again calculated for R_1, R_2, R_3 and R_4 and recorded in Table 23 while Figures 21 and 22 illustrate the hysteresis behaviour of these foams. The high hysteresis means that much energy is absorbed during cyclic deformation and that resilience is low. In comparison therefore, rigid foams exhibit high hysteresis than flexible polyurethane foams.

5.6 Thermal Conductivity of rigid foams

The heat flow and temperature difference across asbestos board is given in Table 24. The rate of heat loss (q_1) obtained from the calibration curve (Figure 23) and the temperature difference (DTs) across the sample were determined and recorded along with measured rate of heat flow(q_m) and rate of heat flow through the sample (q_s) as shown in Tables 25-28. The quantity q_s was calculated from the relation $q_1 = q_m - q_s$.

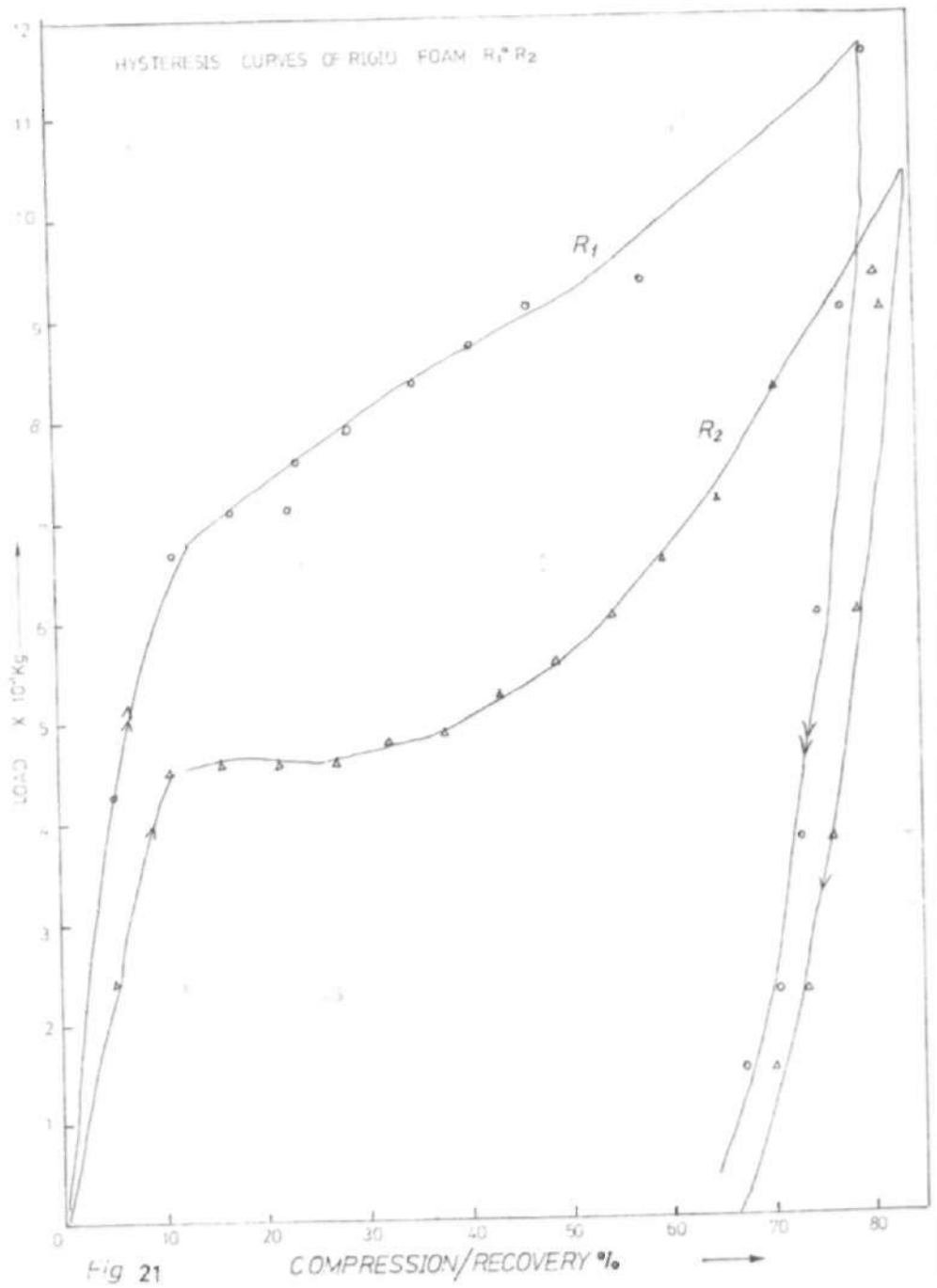

HYSTERESIS CURVES OF RIGID FOAM R1 & R2
R1
R2
LOAD X 10³Kg
0
10
20
30
40
50
60
70
80
COMPRESSION/RECOVERY %

Fig 21

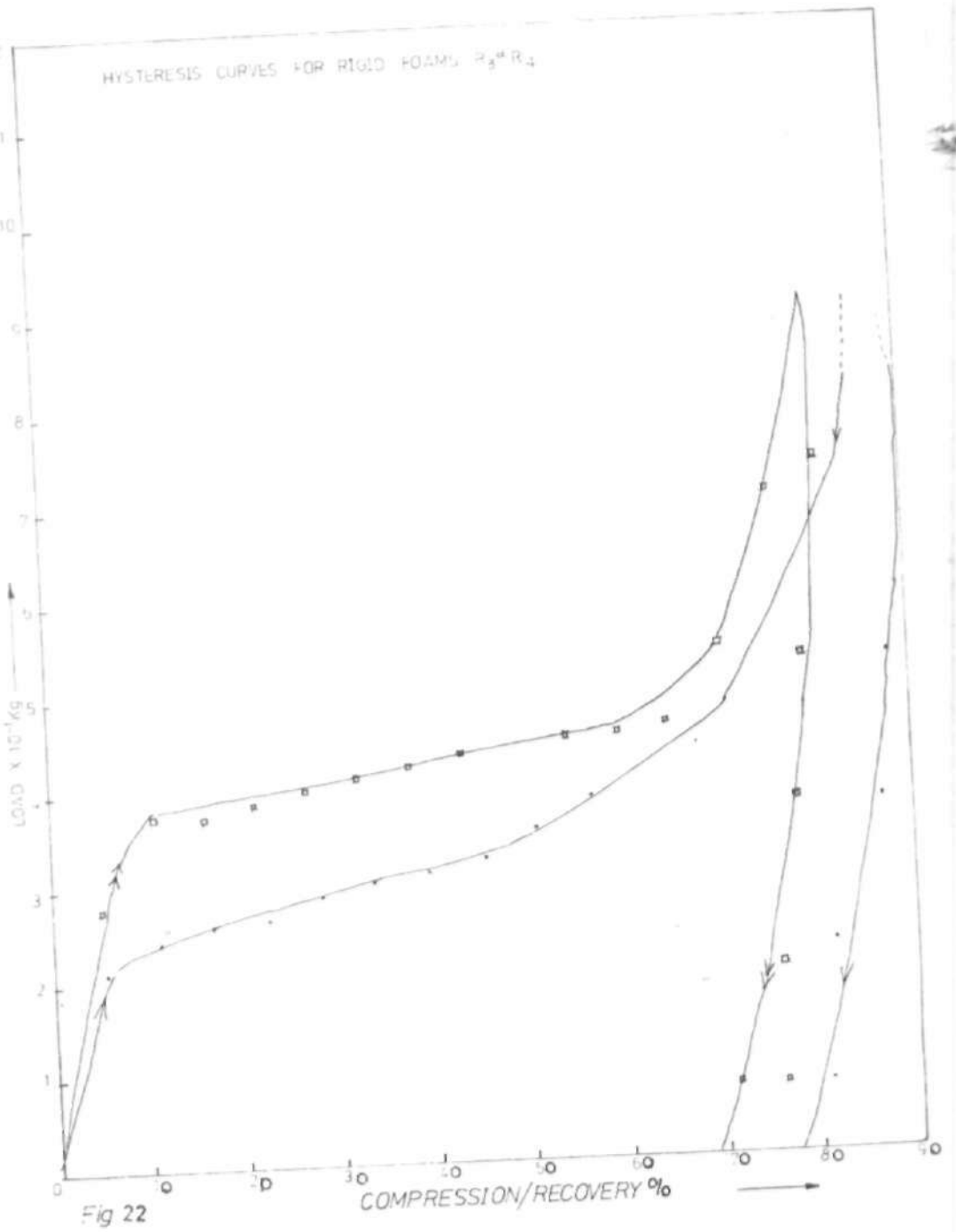

HYSTERESIS CURVES FOR RIGID FOAMS R_3 & R_4
LOAD X 10^{-1} KG
0
1
2
3
4
5
6
7
8
9
10
11
10
20
30
40
50
60
70
80
COMPRESSION/RECOVERY %

Fig 22

Table 22

Yield Indices and step Factors of R_1-R_4

S/No of sample	Density Kgm^{-3}	Load ($Kg/9cm^2$) at				Yield Index
		10%	20%	40%	50%	
R_1	34.59	66.75	70.34	82.58	90.00	1.34
R_2	33.80	43.50	45.90	49.73	60.47	1.39
R_3	30.58	37.50	39.38	42.75	53.25	1.42
R_4	23.06	-	26.55	30.60	34.12	1.47

Table 23

Hysteresis loss of rigid polyurethane foams R_1-R_4

R_1, density = 34.59 kgm^{-3}; R_2, density = 33.80 kgm^{-3};
R_3, density = 30.58 kgm^{-3}; R_4, density = 23.06 kgm^{-3}

Load x 10^{-1} ($kg/9cm^2$)				Compression %			
R_1	R_2	R_3	R_4	R_1	R_2	R_3	R_4
11.25	11.25	-	10.13	77.6	81.5	-	91.0
9.00	9.00	9.00	9.00	77.6	81.5	80.4	91.0
6.00	6.00	5.25	5.25	74.7	78.8	79.3	88.6
3.75	3.75	3.75	3.75	73.0	76.1	78.3	87.5
2.25	2.25	2.25	2.25	70.7	73.1	76.7	82.1
1.49	1.49	0.75	0.75	67.0	69.8	71.7	81.3

Table 24

Head flow and temperature difference across asbestos.

Asbestos Cement

A = 0.0195 m^2

ta = 0.0125 m

K =

q_m W	ΔT_s ^oK	ΔT_b ^oK	q_1 W	q_s W
40	14.0	20.0	23.75	16.25
60	20.50	34.0	39.50	23.80
80	25.0	45.0	51.0	29.0
100	31.0	53.0	64.0	36.0

Table 25

Heat flow and temperature difference across R_1

R_1, density = 34.59 kgm^{-2}

A = 0.0209 m^2

t_a

q_m W	ΔT_s ^oK	ΔT_b ^oK	q_1 W	q_s W
40	28.0	34.0	38.0	2.0
60	42.0	46.0	57.20	2.8
80	59.0	62.5	76.0	4.0
100	79.0	75.0	94.0	6.0

Table 26

Heat flow and temperature difference across R_2

R_2, density = 33.80 kgm^{-2}

A = 0.0209 m^2

t = 5.0×10^{-3} m

q_m W	ΔT_s ^oK	ΔT_b ^oK	q_l W	q_s W
40	28.0	33.0	37.50	2.5
60	57.0	47.0	55.0	5.0
80	69.0	61.0	74.0	6.0
100	97.0	74.0	91.5	8.5

Table 27

Heat flow and temperature difference across R_3

R_3, density = 30.58 kgm^{-2}

A = 0.0209 m^2

t = 5.25×10^{-3} m

q_m W	ΔT_s ^oK	ΔT_b ^oK	q_l W	q_s W
40	22.0	34.0	38.0	2.0
60	35.0	48.0	57.0	3.0
80	50.0	62.0	75.5	4.5
100	65.0	76.0	95.0	5.0

Table 28

Heat flow and temperature difference across R_4

R_4, density = 23.06 kgm^{-2}
A = 0.0209 m^2
t = 5.0×10^{-3} m^2

q_t W	ΔT_s ^oK	ΔT_b ^oK	q_l W	q_s W
40	22.0	33.0	37.75	2.25
60	34.0	48.0	56.7	3.3
80	45.0	61.0	76.0	4.5
100	58.0	75.0	94.5	5.5

Table 29

Thermal conductivity of Rigid foam samples

Sample	Density Kgm^{-2}	Thermal conductivity W/m^oK
R_1	34.59	0.018
R_2	33.80	0.0206
R_3	30.58	0.0211
R_4	23.06	0.0240

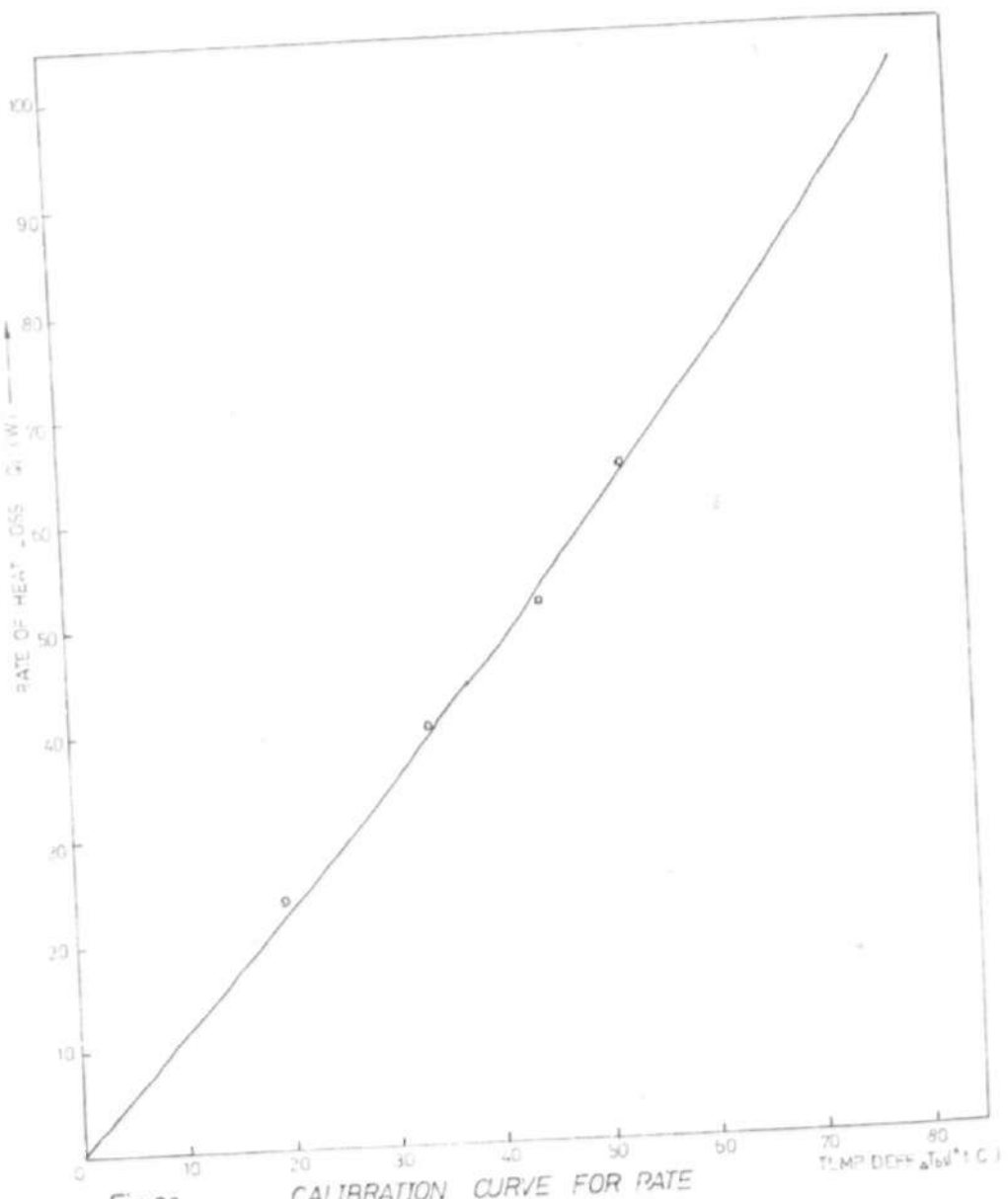


Fig 23 CALIBRATION CURVE FOR RATE OF HEAT LOSS

The plots of q_s versus DTs were then constructed for the various samples as illustrated in Figure 24. From the linear relationship obtained, it can be deduced that the equation $$q_s = KA \frac{DTs}{L}$$ is obeyed. The slope (m) of this curve is equal to KA/L where K = thermal conductivity.

A = area of foam sample (m^2)

L = thickness of sample (metre)

The thermal conductivity values for R_1, R_2, R_3 and R_4 are given in Table 29.

It can be seen from the result presented in Table 29 that there is an increase in thermal conductivity value with increase in freon content and hence decrease in rigid foam density. The total contribution to thermal conductivity is given by $K = K_s + K_g + K_c + K_r$ where s = solid, g = gas, c = convection and r = radiation. If conduction through solid (K_s) were the main contributing factor one would have expected the results to show an opposite trend since the thermal conductivity of freon is much lower than that of the polymer matrix.

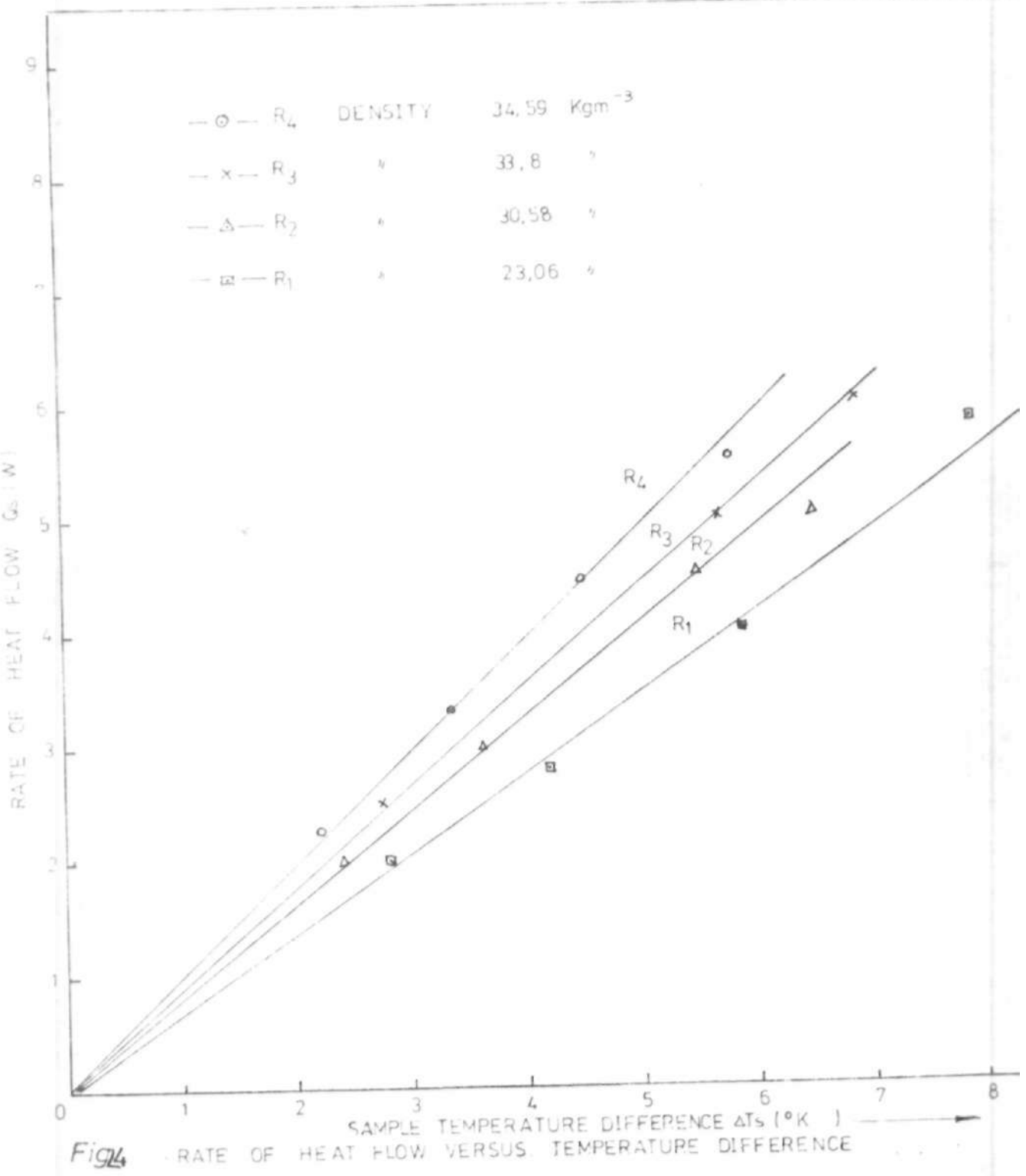


Fig 4 RATE OF HEAT FLOW VERSUS TEMPERATURE DIFFERENCE

It seems therefore that transfer by convection plays a major role in the heat transfer of this system. The void spaces in the foam samples increase with increase in freon content and since each void contains freon vapour, we would expect convection to play a major role. The increase in void spaces would increase heat transfer by convection and this is in agreement with the results obtained.

It can therefore be concluded that the gas phase in a foam sample is generally the largest[36] contributor to the total heat transfer since the gas phase is a major part of the total volume fraction of the rigid foam.

5.7 CONCLUSIONS

The following conclusions were drawn from this work.

i) Excess Tolylene di-isocyanate (TDI) in flexible foam formulation has no significant effect on the physical properties of foams.

ii) Water impurity has a drastic effect on foam properties and should be prevented particularly when tailor made products are desired.

iii) Inclusion of freon as a supplementary blowing agent gives better quality products but of lower densities.

iv) A decrease in the normal amount of water (in-situ blowing agent) used in flexible foam formulations gives foams of higher orders of densities. A drastic decrease in the proportion of water may give semi-rigid products.

v) Increase in rise heights decreases foam densities and surface peeling of upper

part of foam occurs at large rise heights.

vi) Flexible foams of higher yield indices are probably more comfortable in cushioning applications than those of lower yield indices.

vii) Flexible polyether foams have fainly low hysteresis loss and therefore have good resilience.

viii) Rigid polyurethane foams have rather high hysteresis loss and therefore poor resilience.

ix) Within the limits studied, thermal conductivity of rigid foams increase with increase in freon content and hence decrease in density.

APPENDIX I

A.S.T.M D.638-68 Definitions Tensile Parameters.

a. Tensile Stress: The load per unit area of minimum original cross-section, within the gauge boundaries, carried by the test specimen at any given moment.

b. Tensile strength or Ultimate tensile stress(UTS): The maximum tensile stress sustained by the specimen during a tension test.

c. Gauge Length: The original length of that portion of the specimen over which strain or change in length is determined.

d. Elongation: The increase in length produced in the gauge length of the test specimen by a tensile load.

e. Percentage Elongation: The elongation expressed as a percentage of the gauge length.

f. Percentage Elongation at break: The percentage elongation at the moment of rupture of the specimen.

g. Strain: The ratio of the elongation to the product of gauge length and manification factor.

h. Yield Point: The first point on the stress-strain curve at which an increase in strain occurs without an increase in stress.

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