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Amine Aldehyde Condensation Products for Stabilization of Natural Rubber Latex Foam*

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ABSTRACT

The aim of the present paper is to find out a suitable stabilizer for natural rubber latex foam. For this, condensation reactions of formaldehyde with various aliphatic amines and with ethyl chloride were carried out to obtain polyamine-type polymeric products. The resultant products were characterized and evaluated for their stability effects in the natural rubber latex foam. In addition to this, efforts were successfully made to find out an effective formulation to get a foam of maximum strength and durability. The majority of the products synthesized were unable to make the foam stand satisfactorily for a critical duration of time; however, one exhibited an excellent stabilization effect in such foams. It is a triamine-type polymeric base prepared by a new route.

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INTRODUCTION

Rubber industries produce a variety of articles such as tires, textile proofings, footwear, gloves, cushions, pillows, mattresses, corks, and nipples from natural and/or synthetic rubber or natural rubber latex. In addition to padding and other safety devices in automobiles, trucks, subways, trains, and airplanes, there are many important uses of foams or cellular plastics for insulation and in the transport industry. In the preparation of these articles, different types of chemicals are essential. Polyamines and polymeric polyamines play a very important role as vulcanizing agents, accelerators, textile assistants, modifiers of synthetic plastics, and industrial bacteriostatic agents or fungicides [1].

Although polyamines do not represent a distinct class of compounds, they may generally be described as hydrophilic polar substances due to the multiplicity of nitrogen atoms. In acidic or neutral solutions the nitrogen atoms are charged, and in such cases they are soluble in water. Because of their high charge, polarity, and molecular size, polyamines are frequently used in aqueous solutions as stabilizer or flocculants.

The most common method for polyamine synthesis is the reaction between ammonia and ethylene dichloride or epichlorohydrine. Some other important methods are briefly described below.

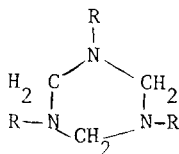
1. Van Alpen [2] condensed 1,3-dibromopropane with ethylenediamine and obtained a short-chain low molecular weight polyamine.

2. Groggins and Shirton [3] noted complex polymer formation as a by-product of the reaction between ammonia and either 1,3-dichloro-2-propanol or epichlorohydrin.

3. Suen et al. [4] described the formation of poly(ethylene polyamines) by the reaction of amine with epichlorohydrin or ethylene halides.

4. Krässig [5] studied the reaction between diamines and formaldehyde to get a syrupy polybismethylene diamine containing hexahydro-s-triazine rings that change on heating into tough transparent gels.

Farbenfabriken Bayer [6] used compounds of the type given below as a cross-linking catalyst for polyurethane foam:



R = Alkyl

The importance of the foams has grown at an unusual rate in the last few years. Several processes have been developed for the

production of natural rubber latex foam. The one developed by Talalay gained much commercial importance after World War II. In spite of difficulties with handling, reproducibility, and less than favorable aging resistance, concentrated natural latex continues to be used today in blends with synthetic latex, where it contributes to wet gel strength, and to resistance and toughness in the final product.

In the present investigation we have studied the synthesis of substituted hexahydro-*s*-triazines from alkylamine/ethyl chloride, ammonia, and formaldehyde. Efforts were made to prepare useful polyamines from 1,3,5-triethyl hexahydro-*s*-triazine (135-TEHT) and to find the best formulation for making an excellent quality of foam. All the polymeric amino products thus synthesized were tested for their foam stability effects in natural rubber latex foam. A few of the properties of these flexible foams were also determined.

EXPERIMENTAL

Technical grade amines were used. Formaldehyde was procured from S.D.S. Lab, Laboratory Chemicals Industry, Bombay, India.

NMR spectra were recorded on a Varian A-60 spectrophotometer using TMS as the internal standard. Viscosities were measured on a Brookfield viscometer. The nitrogen percentage (amine value) was obtained by following an aqueous or nonaqueous method of titration [7].

Condensation reactions of monoamines or diamines with formaldehyde were carried out in benzene solvent. Addition was made at 0 to 10°C, and the mixture was heated as desired (Table 1). Solvent was removed and the products were dried under a reduced pressure of 3 torr.

Ethylamine or ethyl chloride, ammonia, and formaldehyde were mixed to obtain polymeric products after the required heating schedules (Table 2) with a vacuum treatment until constant weight was attained. Some of these reactions were conducted in a sealed metallic bomb.

Polymer (Hy-2) from Hydrazine Hydrate, Ammonia, Ethylamine, and Formaldehyde

In a 500-mL four-necked round-bottomed flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a dropping funnel were mixed 70 g (2.34 moles) paraformaldehyde and about 30 to 40 mL water. They were stirred well and temperature of the flask was maintained at 0°C with the help of an ice-salt mixture. To this, a mixture of ethylamine (21.25 mL, 0.25 mole), ammonia (136 mL of 28% aqueous solution, 2 moles, and hydrazine hydrate (5.8 mL of 54% aqueous solution, 0.1 mole) was added over a period of 40 min. The reaction mixture was stirred at room temperature for 1 hr and

TABLE 1. Reactants, Reaction Conditions, and Properties of Products

Reactants (moles)		Reaction conditions (heating hr at °C)					Yield (%)	% of nitrogen	Comments
Amine	Formal- dehyde	Solvent	0-10	25	50	78			
1. Methylamine, 1	1	Benzene	1	1	1	3	76	25.10	Colorless liquid obtained
2. Ethylamine, 1	1	"	1	1	1	3	81	23.85	" "
3. Propylamine, 1	1	"	1	1	1	3	79	19.10	" "
4. Butylamine, 1	1	"	1	1	1	3	78	15.19	" "
5. Ethylenedi- amine, 1	1	"	0.5	0.5	0.5	3	70	28.80	Red viscous liquid contain- ing amorphous solid obtained. Partly soluble in water
6. Propylene- diamine, 1	2	"	0.5	0.5	0.5	6	68	27.60	Solid product, mp 168, ob- tained. Very slightly soluble in water
7. Hexamethylene- diamine, 1	2	"	0.5	0.5	0.5	3	72	16.50	Asbestos-like solid prod- uct, mp 224-230°C, ob- tained. Insoluble in water
8. Diethylenetri- amine, 1	2	"	0.5	0.5	0.5	3	74	24.10	Reddish viscous product obtained. Soluble in water

TABLE 2. Reactants, Reaction Conditions, and the Properties of Polymeric Products

Reaction no.	Reactants (moles)			Reaction conditions (hr, °C)							Under pressure (40°C/3 mmHg)	Viscosity (cP) ^b	% nitrogen
	Methyl-amine	Ammonia	Formaldehyde	-5	0-10	50	100	150	180	200			
1	1.0	-	1.0	-	1	1	3	5	-	-	1	1,000	12.4
2	1.0	-	2.0	-	1	1	3	5	-	-	1	1,200	11.8
3	1.0	-	4.0	-	1	1	3	5	-	8	1	3,000	6.3
4 ^a	0.1	-	0.1	-	1	1	3	12	-	-	1	8,000	10.4
5 ^a	0.1	-	0.1	-	1	1	3	12	-	-	1	1,500	11.30
6 ^a	0.1	-	0.4	-	1	1	3	5	-	8	1	3,300	6.0
7	1.0	1.0	2.0	-	1	1	20	6	-	3	1	30,500	9.0
8	1.0	3.0	2.0	-	1	1	24	2	-	-	1	3,100	8.50
9	1.0	2.0	3.0	-	1	1	12	6	1	3	1	3,200	8.0
10	1.0	3.0	1.0	-	1	1	88	1	-	-	6	15,000	12.0
11 ^a	1.0	0.2	0.3	-	1	1	12	6	-	3	1	21,000	10.8
12 ^a	1.0	0.9	0.4	-	1	1	4	1	-	1	1	14,000	14.0
<u>Ethyl chloride</u>													
13 ^a	0.1	0.1	0.1	1	1	2	2	2.5	2.5	-	1	17,000	3.0
14 ^a	0.1	0.1	0.5	1	1	2	2	5	5	-	1	19,000	2.35
15 ^a	0.1	0.1	0.5	1	1	2	2	5	5	1	1	20,000	2.30

(continued)

TABLE 2 (continued)

Reac- tion no.	Reactants (moles)				Reaction conditions (hr, °C)							Under pressure (40° C/ 3 mmHg)	Viscosity (cP) ^b	% nitrogen
	Methyl- amine	Ammonia	Formal- dehyde		-5	0-10	50	100	150	180	200			
			0.1	0.2										
16 ^a	0.1	0.2	0.1	0.1	1	1	2	2	10	5	-	1	24,000	2.1
17 ^a	0.1	0.2	0.1	0.1	1	1	2	2	10	5	1	1	24,500	2.0

^aReactions were conducted in a sealed metallic bomb.

^bBy Brookfield viscometer.

then the temperature was raised to 100°C where it was maintained for 4 hr. The temperature of the flask was further raised to 120°C and maintained there for 20 hr. Ultimately the temperature of the flask was raised to 160°C and kept there for 6 hr. The flask was then cooled to get a solid polymer, mp 48 to 53°C.

Dispersions were generally made by grinding the solid fillers in the presence of dispersing agents. Grinding may be accomplished in ball, pebble, or colloid mills.

FOAM PREPARATIONS

Formulation I

Latex (300 g) was placed in the bowl of a Hobart mixer after filtering it through a wet, thin cloth. Potassium oleate soap was added to the latex. It was whipped for 2 to 4 min while ammonium algenate was added. The mixture was again whipped at the highest speed for 45 sec after which 2 or 4 g (50% aqueous solution) of Hy-2 (or other polyamines) was added. The mixture was then whipped at medium speed for 30 sec. At this stage of dispersion, Mixture A was added and the whole mixture was whipped at medium speed for 2 min. The liquid foam thus obtained was poured into a warm mold (40°C) and was put in an oven or water bath at 85 to 90°C for 40 to 60 min. The foam was then removed, washed with water, and dried at room temperature.

Dispersions

Mixture A.

The dispersion of Mixture A was prepared by mixing together the following components in a cylindrical bottle and ball-milling for 48 hr

Zinc oxide	30 g
Sulfur	20 g
Zinc diethyldithio- carbomate (ZDC)	10 g
Dispersing agent	3.2 g (50% aqueous solution)
Ammonium algenate	0.024 g
Water	80.0 g

Mixture B.

In a 2-L capacity cylindrical steel jar, the following components were placed together along with 15 to 20 marble balls:

ZDC	150 g
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Zinc mercaptobenzo- thiazole (ZMBT)	80 g
Sulfur	200 g
Nonox-D	50 g
Belloit-TD	20 g
Water	500 g

The lid of the jar was tightly fixed and the contents were ball-milled for 48 hr.

Mixture C.

In a 500-mL cylindrical bottle, Zinc oxide (100 g), Belloit TD (4 g), and water (96 g) were ball-milled for 24 hr.

Mixture D.

In a 250-mL cylindrical bottle, sodium silicofluoride (50 g), bentonite clay (2 g), and water (48 g) were ball-milled for 24 hr.

Formulation II

In a 1-L one-necked flat-bottomed flask was placed 334 g latex (60%) after filtering it through a wet, thin cloth. Potassium oleate soap (40 g, 20% solution) and the dispersion of Mixture B (20 g) were added and the flask was shaken. It was kept at room temperature for 24 hr.

The latex mass was transferred into the bowl of a Hobart mixer and whipped for 2 min at various speeds. After effective frothing, 2 and/or 4 g Hy-2 (50% aqueous solution) and/or other polyamines were added as a stabilizer with continuous whipping for 2 more min. At this stage 20 g of the Mixture C dispersion was added followed by 4 g of the Mixture D dispersion. This was whipped for an additional 2 min at medium speed. The liquid foam obtained was poured into a warm mold (40°C). The mold containing the foam was kept in an oven at 70°C for 15 min and then dipped in a boiling water bath for 1 hr. The foam was removed, washed with water, and dried at room temperature.

RESULTS AND DISCUSSION

In earlier work [8] the reactions of aliphatic as well as aromatic aldehydes with aniline to get diamine compounds were described. The significant aspect of these reactions was that the primary amino groups remained intact in the final products. However, in the present studies primary amino groups of aliphatic amines themselves took part in the condensation reactions with formaldehyde to produce water-soluble polyamines as end products.

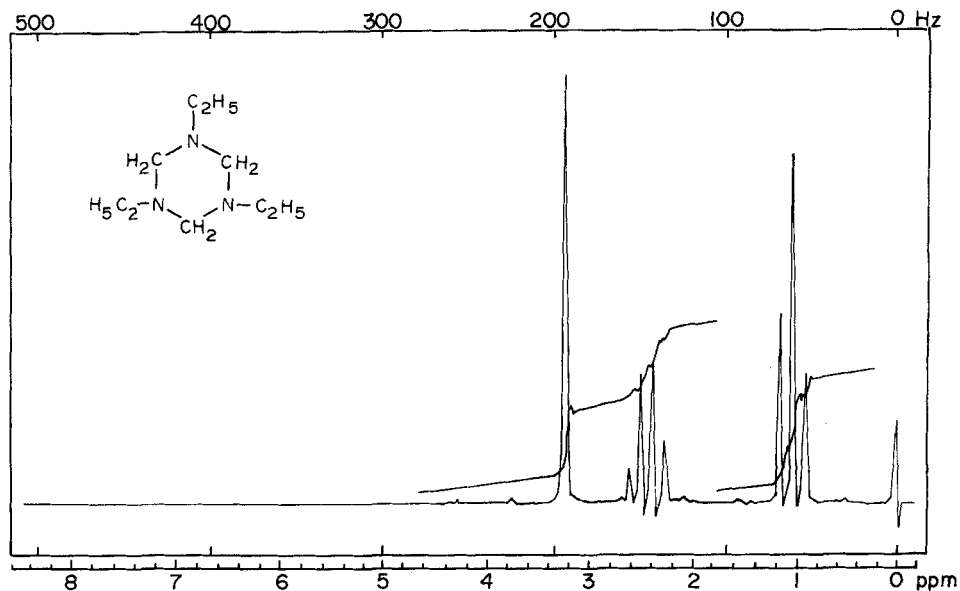


FIG. 1. NMR spectrum of 1,3,5-trimethylhexahydro-s-triazine.

Thus aliphatic monoamines such as methylamine, ethylamine, n-propylamine, and n-butylamine were reacted with formaldehyde at a 1:1 molar ratio to produce 1,3,5-trimethyl-, 1,3,5-triethyl-, 1,3,5-tripropyl-, and 1,3,5-tributyl hexahydro-s-triazines, respectively (Reactions 1-4, Table 1). All of these hexahydro-s-triazines were obtained in yields above 76%. They were colorless liquids with an irritating odor. The NMR spectra of these products were recorded in carbon tetrachloride using TMS as the internal standard. As an illustration, the NMR spectrum of 1,3,5-triethylhexahydro-s-triazine (135-TEHT) is given in Fig. 1. It shows a triplet at $\delta = 0.83-1.16$, a quartet at $\delta = 2.16-2.60$, and a strong triplet at $\delta = 3.20$.

Diamine-formaldehyde reactions, however, produced viscous liquids to solid end products of comparatively low yield compared to the monoamine-formaldehyde reactions.

Table 2 describes the reactants, the reaction conditions, the percentage of nitrogen, and the viscosities of all the end products obtained from alkyl amine/and or chloride, ammonia, and formaldehyde. It can be seen that longer heating is required to produce end products with higher viscosities. The presence of ammonia has a profound effect on obtaining good polymeric products (Reactions 7-12, Table 2). In Reactions 13 to 17 ethylamine was replaced by ethyl chloride which was generated from ethyl alcohol, concentrated hydrochloric acid, and zinc chloride at the boiling steam bath temperature. It was collected

TABLE 3. Reactants, Reaction Conditions, and Properties of the Polymeric Products^a

Reaction no.	Reactants (moles)		Reaction conditioning (hr of heating)						Under reduced pressure (3 mmHg minim at 40°C)	Viscosity (cP) ^b	% nitrogen
	1,3,5-TEHT	Ammonia	50	100	150	200	250	270			
1	0.1	0.025	1	1	1	-	-	-	10	35	15.0
2	0.1	0.050	1	1	1	1	-	-	10	60	8.3
3	0.1	0.10	1	1	1	1	1	-	10	100	7.3
4	0.1	0.15	1	1	1	1	-	5	10	800	7.0
5	0.1	0.20	1	1	1	1	15	-	10	27,000	6.24
6	0.1	0.30	1	1	1	5	20	-	10	23,000	5.0
7	0.1	0.40	1	1	1	1	5	10	10	16,000	4.0
8	0.1	0.40	1	1	1	5	10	10	10	14,000	3.0
9	0.1	0.50	1	1	1	5	10	10	10	14,000	3.0
10	0.1 KOH	0.50 g	1	1	1	-	-	-	10	40	14.0
11	0.1	0.50	1	1	1	10	-	-	10	200	6.2

^aAll the reactions were carried out in a sealed metallic bomb.^bBy Brookfield viscometer.

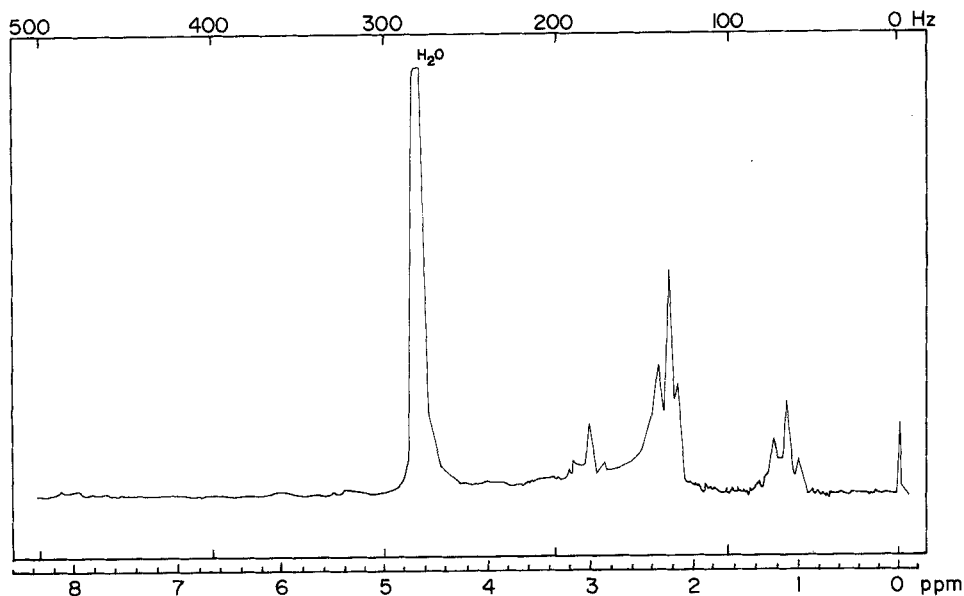


FIG. 2. NMR spectrum of Hy-2.

at -20°C . All five reactions involving ethyl chloride were conducted in sealed metallic bombs because of the low boiling point (13°C) of ethyl chloride. The total removal of HCl from the final product was difficult, and its presence caused a reduction of the practical titre value of acid quantity required when the weigh amount of product was titrated against perchloric or hydrochloric acid.

Ring-opening polymerization reactions of the triazine-type nucleus have been proposed by Grundsmann and Alfred [11]. In recent times, studies on ring-opening polymerization of azitidine [12], conidine [13] and 1,3,3-trimethylazitidine [14] have been reported by various authors [15]. In the present work, efforts were made to polymerize 1,3,5-triethylhexahydro-*s*-triazine in the presence of either ammonia or potassium hydroxide by the sealed metallic bomb route. At low temperatures thin liquids were obtained, indicating less or no polymerization (Reactions 1-4, Table 3). However, when longer heating schedules were followed with an increase in the molar proportion of ammonia, polymers with increased viscosities and hence higher molecular weights were obtained.

Only one polymer, designated as Hy-2, could be obtained from hydrazine hydrate, ethylamine, ammonia and formaldehyde. Hy-2 was prepared at 100°C and above, and remained in the liquid state at high temperatures. However, cooling yielded a solid mass. Its molecular weight as measured by mass spectrometry was found to be 570. The NMR spectrum (Fig. 2) recorded in H_2O showed a small

triplet at $\delta = 0.93-1.23$, a strong triplet at $\delta = 2.13-2.50$, and a singlet at $\delta = 3.03$.

The development of foam in the late 1920s was an attempt to replace sponge rubber which required heavy mastication and could only be made in batches at high density and had poor uniformity. Foaming became a commercial process only after the development of the two-step method by Dunlop [9, 10] which consisted of dispersion of air in a latex followed by controlled coagulation or gelation to produce a foam. Foam is made from latex and consists of rubber particles stabilized by soap or other surface-active materials which are mechanically mixed with air. The final mixture is nothing but a froth in which surface-active agents stabilize both the surface of the rubber particles and the air-water interface. For good gelation it is necessary to decrease the stabilization of polymer surface to effect agglomeration of rubber particles before the stability of the air bubbles becomes low enough to cause rupture.

Gelation, an important phenomenon in foam production, can be achieved by two different chemical systems:

1. Heat gelling (Kayasam process)
2. Room temperature gelling (Dunlop process)

In heat gelling, an ammonium salt is used in combination with zinc oxide. When a latex compound is heated, ammonia is driven off, producing an acid environment in which the latex particles are destabilized. Zinc is chelated by ammonia to form several zinc-ammonium complexes. At high pH, quaternary chelate is the most likely species. The quaternary chelate does not destabilize the latex particles, and thus the system is stable at room temperature. After heating, ammonia is driven off and lower amine chelates are formed which react with the surface-active agents. Also, in the presence of zinc chelate, the surface tension of a soap solution is sufficiently low that air bubbles remain stable and a closed cell foam results.

In the Dunlop room temperature gelling process, chemicals such as sodium silicofluorides are used in combination with zinc oxide to produce gelling. In the presence of water, sodium silicofluoride decomposes to yield hydrogen fluoride and silicic acid. As the pH is reduced, both decomposition products and zinc oxide destabilize the surface-active agents. This kind of gelation results in an open cell foam.

The basic compounding ingredients for foam are (1) latex, (2) a foaming agent such as soap, (3) a vulcanizing agent, (4) an antioxidant, (5) a filler, (6) a sensitizer, (7) zinc oxide dispersion, and (8) ammonium chloride or sodium silicofluoride as the gelling agent.

Although a number of methods have been developed for making foams, the one which has attained the most important commercial development involves whipping the latex in a bowl with a foaming agent. The mixture is then foamed to any desired degree, after which a gelling agent having a delayed action and the vulcanization mixture are added.

TABLE 4. Properties of a Latex Foam

	Formulation I Hy-2		Formulation II Hy-2	
	2 g	4 g	2 g	4 g
Density, lb/ft ³	32	34	38	40
Tensile strength lb/in. ²	500	550	600	635
Elongation	130	140	160	170
Shore hardness A	45	50	55	60
Compression load at 50% deflection, lb/in. ²	650	675	700	750

By adjusting the quantity of gelling agent, stabilizer, and the temperature at which the mixing is done, the foam may be whipped and introduced into a warm mold. The mold is then closed and adjusted to the vulcanizing temperature for a period of 20 to 60 min as necessary. After this period the foam may be recovered, washed, and dried.

In the present studies all the requirements described above were followed. Polyamine products synthesized by various reactions were used as the foam stabilizers in the latex foam preparation. Two different formulations (mentioned above) were developed to prepare the foams. Only Hy-2 stabilized the latex foam effectively. In all other cases the foam either collapsed immediately or gelled after a very short period. Since all other conditions were kept the same, the stabilizer was the only factor responsible for a good foam. In Table 4 the properties of the foams that were prepared by using Hy-2 stabilizer are described. They are quite comparable to the properties of foams available commercially.

While both formulations gave a good quality of foam, Formulation II yielded a relatively better cell structure and a foam of rather superior quality. Photographs of foams using Hy-2 (2 g and/or 4 g) are presented as Fig. 3. Mechanical strength and other properties of the foams show the clear superiority of Formulation II over Formulation I.

Figure 4 shows a simple compression deflection curve of a low density latex cushion foam obtained using Formulation II and is self-explanatory.

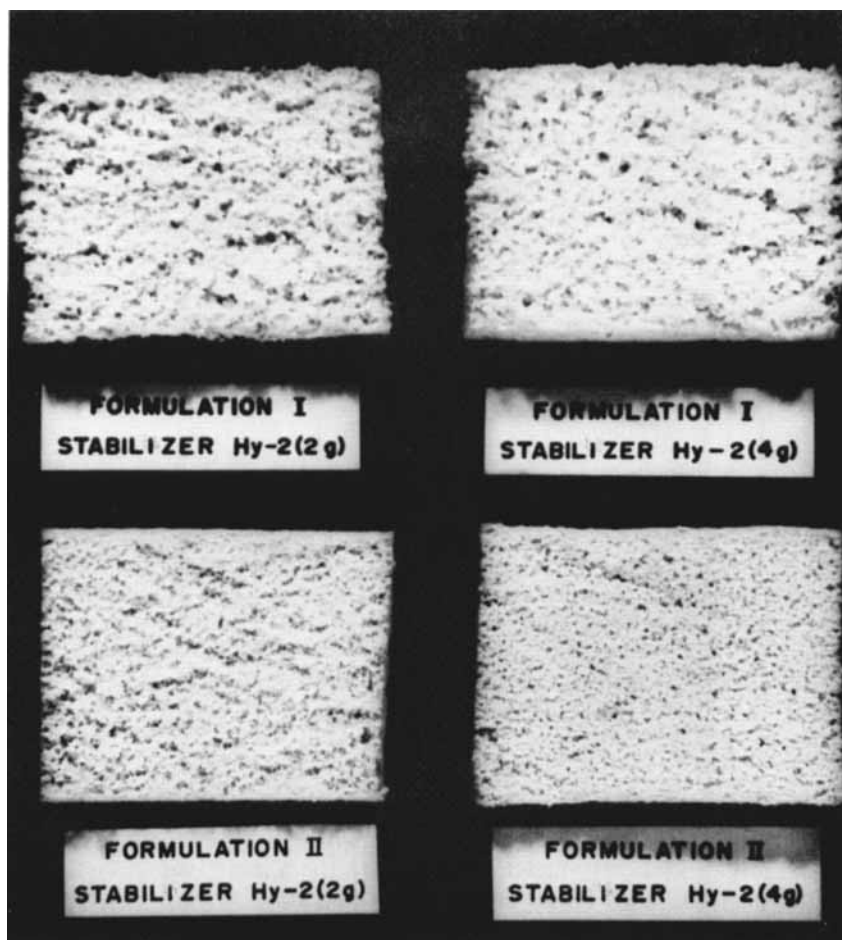


FIG. 3. Photograph of foams.

CONCLUSION

1. In practice, it has been found that the greater the production rate and the lower the density of the foam, the more difficult it is to obtain a product with a homogeneous cell structure and uniform density.
2. Hy-2 is the only effective polyamine of all the products synthesized.
3. Formulation II has a better potential for producing a foam with higher quality than has Formulation I.

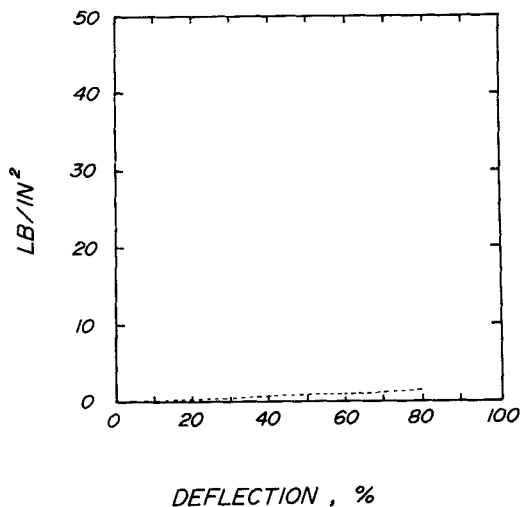


FIG. 4. Compression-deflection curve of the latex foam.

4. If the quantity of Hy-2 stabilizer is increased beyond the values mentioned above, the change in the properties of the foam was not significant.

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