Urethane Foams From Animal Fats: V. Flame Resistant Foams From Hypohalogenated Glycerides[1]

F. SCHOLNICK, E. J. SAGGESE, A. N. WRIGLEY and G. R. RISER,
Eastern Utilization Research and Development Division,[2] Philadelphia, Pennsylvania 19118

Abstract

A series of urethane foams has been prepared using hypohalogenated derivatives of triolein, monoolein, lard and tallow as the polyol ingredient. Two-step hypohalogenation was achieved by epoxidation of the glyceride, followed by treatment with HX. One step hypohalogenation was effected by direct addition of hypochlorous acid (from calcium hypochlorite) or hypobromous acid (from N-bromoacetamide). The polyols, which varied from viscous liquids to semi-solids, were adjusted in equivalent weight with triisopropanolamine. Urethane foams were prepared from the adjusted polyols using polymeric polyisocyanate as the isocyanate, triethylene diamine catalyst and Freon 11 as blowing agent. Additional foams were made with 2% antimony oxide as an added fire retardant. Rigid foams were obtained from each glyceride polyol. Fire retardant properties were measured using a modification of ASTM Method D1692-59T. In each case, the foams exhibited greater flammability resistance than those obtained from polyols containing no halogen atoms. It was noted that the presence of antimony oxide was necessary in order to attain nonburning foams but was accompanied by a lowering of compressive strength.

Introduction

The preparation of rigid urethane foams from fatty polyols has been the subject of a number of contributions from this laboratory (1–4). Most recently, foams have been prepared from polyols obtained by hydration of epoxidized glycerides (4). Epoxidized glycerides including triolein, monoolein and lard were hydrated using 24% fluoboric acid as catalyst. The resulting polyols were adjusted in equivalent weight and were foamed in prepolymer and one step systems. Foam properties were then evaluated; however it was noted that all the foams burned readily.

Because of the growing importance of fire resistant urethanes, it was considered desirable to prepare polyols having halogen atoms incorporated in the molecule. Foams prepared from such derivatives would be expected to be less flammable and more resistant to oxidation (5). In the work currently reported, fat-based polyhydroxy compounds containing halogen atoms were obtained by two methods:

(a) Reaction of epoxidized glycerides with dilute hydrobromic or hydrochloric acid. As shown in Figure 1, treatment of epoxidized triolein with HX should lead to formation of a triol containing three halogen atoms. Epoxidized glycerides including triolein, lard, tallow and monoolein were converted to their hypohalogenated derivatives using this scheme.

(b) Analogous polyols could be obtained by the direct addition of hypochlorous or hypobromous acid to the unsaturated glycerides. Hypochlorous acid was liberated from calcium hypochlorite by acidification with carbon dioxide. Hypobromous acid was prepared from N-bromoacetamide by addition of water.

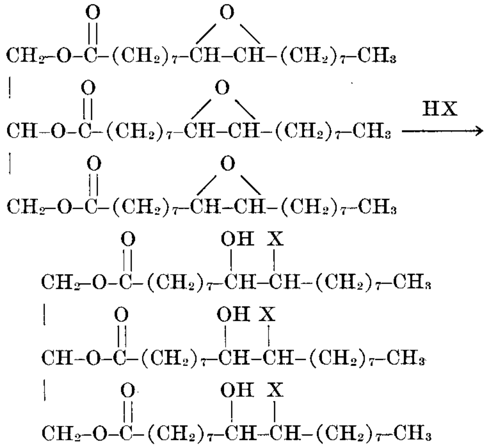

FIG. 1. Epoxidized triolein and hypohalogenated derivative (one isomer illustrated).

All of the hypohalogenated glycerides were liquid or semisolid and had sufficient hydroxyl functionality to make them suitable for urethane foam formation. They were adjusted in equivalent weight and used in one step systems with polymeric polyisocyanate (PAPI) as the isocyanate.

Experimental Procedures

The materials listed below were used as received: Glyceryl trioleate, over 90% purity (Hormel Institute), iodine value 84.8 (found); glyceryl monooleate (Eastman Organic Chemicals), iodine value 66.4 (found); lard (Armour and Co.), iodine value 57.3 (found); tallow, fancy (Wilson-Martin Chemical Corp.), iodine value 51.3 (found); calcium hypochlorite, purified, 30–35% available chlorine (J. T. Baker Chemical Company); N-bromoacetamide (Aldrich Chemical Company), mp 108–109 C.

Procedures

Preparation of Hypohalogenated Glycerides. From Epoxidized Glycerides: Glycerides which had been epoxidized by peracetic acid using conventional techniques (6) were dissolved in dioxane, and an excess of dilute (24%) HBr or HCl was added dropwise with stirring. After 1 hr the mixture was diluted

TABLE I
Hypohalogenated Glycerides
(HX Addition to Epoxidized Glycerides)

Epoxidized glyceride	HX	Per cent hydroxyl		Per cent halogen		Per cent oxirane	
		Theor.[a]	Found	Theor.[a]	Found	Initial	Residual
Lard	HCl	3.43	3.16	7.15	6.96	3.31	0.07
	HBr	3.15	3.26	14.80	15.20	3.31	0.02
Tallow	HCl	3.11	3.31	6.48	6.12	2.91	0.06
	HBr	2.88	3.13	13.51	9.46	2.91	0.06
Monoolein	HCl	12.29	9.80	8.15	6.69	4.00	0.06
	HBr	11.15	8.93	16.67	15.92	4.00	0.06
Triolein	HCl	4.83	4.54	10.07	10.82	5.09	0.08
	HBr	4.29	4.13	20.17	18.28	5.09	0.07

[a] Based upon original iodine value.

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[2] ARS, USDA.

TABLE II
Hypohalogenated Glycerides
(Direct Addition of HOX)

Glyceride	HOX	Per cent hydroxyl		Per cent halogen		Residual iodine value
		Theor.[a]	Found	Theor.[a]	Found	
Lard	HOCl	3.43	1.60	7.15	14.30	2.1
	HOBr	3.15	2.26	14.80	13.42	1.0
Tallow	HOCl	3.11	2.04	6.48	14.15	1.8
	HOBr	2.88	2.48	13.51	12.26	0.6
Monoolein	HOCl	12.29	6.22	8.15	14.28	0.8
	HOBr	11.15	9.59	16.67	16.97	0.4
Triolein	HOCl	4.83	2.13	10.07	18.92	3.8
	HOBr	4.29	3.48	20.17	21.62	0.1

[a] Based upon original iodine value.

with water and extracted with several small portions of chloroform. The extracts were washed acid free, dried over magnesium sulfate and the solvent removed. A summary of the analytical data obtained is given in Table I.

Direct Hypohalogenation: The general procedure used for hypochlorination is illustrated with lard. Fifty grams of lard (0.12 mole of olefinic unsaturation) was suspended in 1000 ml water with 0.5 g of an alkylbenzenesulfonate and 35.8 g (0.20 mole) of calcium hypochlorite dihydrate. Carbon dioxide was bubbled through the stirred mixture at room temperature for 24 hr. An additional 0.20 mole of calcium hypochlorite was added, and the reaction was continued for an additional 12 hr. The mixture was filtered and the precipitate extracted with four 100 ml portions of chloroform. The extracts were washed with 2% sodium bicarbonate, then with water and dried over magnesium sulfate. Removal of the chloroform led to isolation of 54.5 g of product.

Direct hypobromination was effected by use of N-bromoacetamide and the general procedure is illustrated with lard. Fifty grams of lard (0.12 mole of olefinic unsaturation) was dissolved in 250 ml dioxane and 50 ml water. A solution of 24.8 g (0.18 mole) of N-bromoacetamide in 250 ml dioxane was added dropwise with stirring at room temperature. The mixture was stirred 2.0 hr, diluted with water, and extracted with four 50 ml portions of chloroform. The extracts were washed with 2% sodium bicarbonate, then with water and dried over magnesium sulfate. Removal of solvent led to isolation of 62.7 g of product.

A summary of analytical data obtained from the hypohalogenated glycerides prepared by direct addition of HOX is given in Table II. Percent hydroxyl found in HOCl polyols approximated only half the theoretical, while per cent chlorine was almost double the expected amount. However, the formation of dihalides as by-products of addition of HOCl to alkenes is commonly observed (7) and would explain the discrepancy in analyses. Per cent hydroxyl and bromine in HOBr polyols prepared by use of N-bromoacetamide agreed in general with theoretical values. Comparison with Table I indicates that more efficient hydroxylation was achieved by use of the two step process rather than direct addition of hypohalous acids.

TABLE III
Typical Foam Formulation

Component	Weight, g	Percentage (exclusive of blowing agent)
Polyol (epox., triolein + HBr)	5.50	22.53
Triisopropanolamine	4.50	18.43
Silicone L-520	0.16	0.65
Dabco-33	0.45	1.84
Freon-11	4.10	....
PAPI	13.80	56.53

Foam Preparation. The hypohalogenated glyceride was adjusted to an equivalent weight of 120 by addition of triisopropanolamine. Ten grams of the polyol mixture was mixed with a polymeric polyisocyanate (PAPI), silicone oil, triethylenediamine catalyst (DABCO-33) and blowing agent (Freon-11). A typical formulation is given in Table III. In additional formulations 2% antimony oxide was used in order to increase fire retardance.

Test Methods. Density, compressive strength (at 10% compression) and percentage of open cells were measured by methods described previously (1). The relative flammability characteristics of the foams were evaluated using ASTM Method D-1692 modified for convenience and economy. A small sample 50 mm long, 37 mm wide and 13 mm high was marked 10 mm from each end and was supported upon a metallic screen. The latter was clamped horizontally to a ring stand. A microburner, whose flame height was adjusted so that the uppermost edge just impinged on the sample, was employed as a flame source. The flame was brought into contact with the sample and permitted to remain there for 30 sec or until the flame front reached the first gauge mark, and then removed.

If no evidence of ignition, such as flame spread or progressive glow, was seen after removal of the burner flame, the sample was rated "nonburning." If the specimen continued to burn after removal of the flame, a stop watch was started when the flame front reached the first gauge mark and stopped when the flame front reached the second gauge mark. A sample which reached the second gauge mark was rated "burning." If the sample showed evidence of ignition and burned upon exposure to the flame but

TABLE IV
Physical Properties of Foams (HX Process)

Polyol source	Additive	Density, lb./ft^3	Compressive strength, PSI	Open cells, %	Burning rate, cm/min	Rating[a]
Epoxidized Lard + HCl	....	1.84	18.5	79.4	6.7	B
	Sb_2O_3	2.04	17.0	74.9	5.3	SE
Epoxidized Lard + HBr	....	2.10	14.0	95.0	3.8	B
	Sb_2O_3	2.29	11.5	97.4	2.6	SE
Epoxidized Tallow + HCl	....	1.78	17.0	25.5	5.6	B
	Sb_2O_3	1.82	16.5	31.7	4.0	SE
Epoxidized Tallow + HBr	....	1.90	20.0	24.6	3.4	B-SE
	Sb_2O_3	1.93	18.0	24.9	2.7	SE
Epoxidized Monoolein + HCl	....	1.86	14.0	22.7	7.0	B
	Sb_2O_3	1.88	12.0	29.3	1.7	NB
Epoxidized Monoolein + HBr	....	1.88	12.5	28.8	5.6	SE
	Sb_2O_3	1.81	10.0	26.3	0.7	NB
Epoxidized Triolein + HCl	....	1.89	28.5	16.7	5.2	B-SE
	Sb_2O_3	1.89	24.0	17.3	2.5	NB
Epoxidized Triolein + HBr	....	1.87	16.0	24.0	4.7	SE
	Sb_2O_3	1.86	15.0	21.7	3.2	SE

[a] B, burning; SE, self-extinguishing; NB, nonburning.

TABLE V
Physical Properties of Foams (HO-X Process)

Polyol source	Additive	Density, lb./ft^3	Compressive strength, PSI	Open cells, %	Burning rate, cm/min	Rating^a
Lard + HOCl	....	2.14	9.5	99.0	3.3	B
	Sb_2O_3	2.28	8.5	99.1	1.2	NB
Lard + HOBr	....	2.20	7.7	99.1	2.7	B
	Sb_2O_3	2.26	6.0	98.0	1.0	NB
Monoolein + HOCl	....	1.59	20.0	16.7	2.2	SE-NB
	Sb_2O_3	1.66	19.0	23.4	1.5	NB
Monoolein + HOBr	....	1.72	15.5	19.5	1.6	NB
	Sb_2O_3	1.64	13.0	27.2	1.3	NB
Triolein + HOCl	....	1.77	14.0	99.7	4.1	B
	Sb_2O_3	1.79	11.5	99.9	1.8	NB
Triolein + HOBr	....	2.00	18.0	30.1	1.0	NB
	Sb_2O_3	1.68	17.0	24.3	0.7	NB

[a] B, burning; SE, self-extinguishing; NB, nonburning.

did not burn past the second gauge mark, it was rated to be "self-extinguishing." Rate of burning was determined and the apparent cause for extinguishing was noted.

This small scale test is only useful to determine the relative flammability of the materials. This test was not intended to measure suitability for large scale application. It was economical in that it required little time, a small sample and simple apparatus.

Discussion

A summary of the physical properties of the prepared foams is given in Tables IV and V. Table IV illustrates the properties of foams derived from polyols obtained by the HX process. Densities ranged from 1.78 to 2.29 lb./ft.^{3} In general, higher compressive strengths were exhibited by foams prepared using HCl instead of HBr and contained a lower amount of open cells. As observed previously (8), the presence of antimony oxide was invariably accompanied by lower compressive strengths.

The properties of foams prepared from one step hypohalogenated glycerides are given in Table V. Urethanes derived from monoolein and triolein were comparable to those formed from HX polyols. However, foams from lard and tallow one step polyols were inferior in compressive strength to those from HX polyols. In fact, foams derived from tallow collapsed and were consequently not tested or reported in Table V.

It is believed that inferior physical properties in urethanes are caused by the presence of excessive contaminants. Purification of polyols prior to their use should lead to formation of foams with improved properties. This approach is currently under investigation in our laboratory.

A summary of flammability test results is included in Tables IV and V. In all tests performed no shrinkage or curling was evident upon heating, nor was any dripping or melting observed. Smothering of flame by production of heavy char was the primary mode of extinction. A number of foams burned with little or no smoke, while others emitted dark, dense fumes. As anticipated, the use of hypohalogenated glycerides as polyols led to foams with superior flammability resistance as compared to those prepared previously from oxyalkylated dihydroxystearic acid or hydrated epoxidized glycerides (4). The latter foams contained no halogen and burned completely at a very rapid rate under conditions of this test. The burning was accompanied by dripping and melting.

With the foams currently reported, addition of antimony oxide was necessary in order to achieve a nonburning rating. In most cases, the foams from HBr were slower burning than those from HCl polyols. Analogous results were also obtained in the HOCl and HOBr series.

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