Solvent-Blown Rigid Urethane Foams from Castor-Based Polyols[1]

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The preparation of trichlorofluoromethane-blown rigid urethane foams using toluenediisocyanate and castor oil-derived polyols was investigated. The castor-based polyols included castor oil, hydroxylated castor oil, technical glycerol-, pentaerythritol-, and sorbitol monoricinoleates, and N,N-*bis*(2-hydroxyethyl)ricinoleamide.

The last of these yielded the best foams when used as the sole polyol component added to the prepolymer. However better foams were obtained by using, as the polyol component, a mixture of a castor oil-derived polyol and a lower-molecular-weight polyol with a higher hydroxyl content. These polyol mixtures yielded more highly cross-linked polymers and hence foams with higher compressive strengths and less tendency to shrink after foaming.

The effect of catalyst, silicone surfactant, and trichlorofluoromethane content was also investigated. An empirical relationship between density and compressive strength in a given foam system was derived.

THE PREPARATION of urethane foams from castor oil and castor-based polyols has been described in recent publications (1–4). These foams were prepared by a two-step process in which a castor-based polyol was first reacted with excess polyisocyanate to form an isocyanate-terminated polyurethane prepolymer. Reaction of this prepolymer with water in the presence of a catalyst caused chain extension and cross-linking and was accompanied by the evolution of carbon dioxide which expanded or blew the plastic to a foam.

The foams studied in the present investigation were also prepared by a two-step procedure, but the isocyanate-terminated prepolymer was extended and cross-linked by reaction with castor-based polyols, and blowing was caused by vaporization of a low-boiling solvent, trichlorofluoromethane (b.p. 24°C.), by the heat of the polymerization reaction. The practice of blowing urethane foams by vaporization of trichlorofluoromethane is being increasingly adopted by manufacturers of these foams because of savings in material costs and the superior thermal insulating properties of the resulting foams.

In this investigation the utility of several castor-based polyols for the preparation of solvent-blown urethane foams was evaluated. The important variables, including polyol and prepolymer composition and concentration of catalyst, surfactant, and blowing agent, were studied in order to develop optimum procedures for preparation of these foams.

Experimental

Materials. N,N-*bis*(2-hydroxyethyl)ricinoleamide was prepared by reacting methyl ricinoleate with diethanolamine. A mixture of 312.5 g. (1.0 mole) of methyl ricinoleate, 126.5 g. (1.2 moles) of diethanolamine, and 63 ml. (0.05 mole) of 0.8 N sodium methoxide in methanol was stripped to constant weight under aspirator vacuum at 50°C. The product was taken up in 300 ml. of ethyl acetate and washed successively with 300 ml. of N HCl, three 350-ml. portions of 20% NaCl, 200 ml. of M K_2CO_3, two 200-ml. portions of 20% NaCl, and 300-ml. portions of water until the solution started to emulsify. The solvents were then stripped under aspirator vacuum at 70–80°C. with the addition of benzene to remove water azeotropically. Drying at 80°/0.7 mm. Hg afforded 376 g. (97% yield) of a pale yellow oil. A 250-g. portion of this crude product was dissolved in 860 ml. of methanol and passed slowly through a mixed bed ion exchange resin column [30 g. of Dowex 50 (H^+ form) plus 30 g. of Dowex 1 (OH^- form)]. Removal of the solvent and drying at 60°/1 mm. Hg yielded 242 g. of neutral N,N-*bis*(2-hydroxyethyl)ricinoleamide (OH value: calcd. 436, found 432).

Sorbitol monoricinoleate was prepared by reaction of sorbitol and methyl ricinoleate in dimethylformamide essentially according to a published procedure for the preparation of sucrose monoesters (5) except for the substitution of a molar equivalent of sorbitol for sucrose. From 118 g. of methyl ricinoleate and 206 g. of sorbitol there were obtained 142 g. (81% yield) of crude sorbitol monoricinoleate (OH value: calcd. 727, found 545; acid value 4.4) as a soft waxy solid.

Other materials used were commercially available products. These included:

glycerol monoricinoleate (Baker Castor Oil Company, Flexricin 13)
pentaerythritol monoricinoleate (Baker Castor Oil Company, Flexricin 17)
glycerol mono-12-hydroxystearate (Baker Castor Oil Company, Paricin 13)
hydroxylated castor oil (Baker Castor Oil Company, Estynox 351)
N,N,N′,N′-tetrakis(2-hydroxypropyl)ethylenediamine (Wyandotte Chemicals Corporation, Quadrol)
trimethylolpropane, TMP (Celanese Corporation)
toluenediisocyanate (TDI), 80% 2,4- and 20% 2,6-isomers (E. I. duPont de Nemours and Company, Hylene TM)
trichlorofluoromethane, CCl_3F (Allied Chemical Corporation, Genetron 11)
triethylenediamine (Houdry Process Corporation, Dabco)
stannous octoate (Nuodex Products Company, Nuocure 28)
triethylamine (Eastman)
silicone oil (Union Carbide Corporation, L-520)

Prepolymer Preparation. The standard prepolymer, used for the preparation of all foams unless specified otherwise, was prepared by agitating for 1 hr. at 75°C. under nitrogen a mixture of 32.8 g. of pentaerythritol monoricinoleate, 32.8 g. of trimethylolpropane, and 254.2 g. of toluenediisocyanate (80% of 2,4- and 20% of 2,6-isomer). Slight cooling in a water bath was required during the initial part of the reaction. The product, a viscous amber oil (25.7% isocyanate, viscosity at 25°C. = 901 poises), was stored under nitrogen in a tightly-sealed jar.

Foam Preparation. All foams were prepared by reacting an isocyanate containing prepolymer with a polyol or polyol mixture, using an NCO/OH ratio of 1.00 and a total polymer weight of 10.0 g. (not

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[2] A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

including blowing agent, catalyst, and surfactant). The prepolymer was weighed into a 9-oz. hot-drink paper cup and mixed with 0.04–0.2 g. of L-520 silicone oil and 1.5 g. (unless specified otherwise) of trichlorofluoromethane. To this solution was added a previously prepared mixture of the polyol with catalyst (0.06 g. of Dabco unless specified otherwise). The two solutions were mixed rapidly with a spatula for about 15 seconds, then permitted to foam. The foams were allowed to stand for a day at room temperature before they were removed from the cups and sampled for testing.

Test Methods. Foam time was recorded as the time between the completion of mixing and the attainment of maximum foam height.

Horizontal slices 1 in. thick were cut from the foams. Further tests were run on cylindrical pellets cut from these slices. Values reported are averages obtained from the top and bottom of each foam.

The density was determined by weighing cylindrical pellets of foam 1.00 in. in height with a diameter of 1.625 in.

Compressive strength was determined on the pellets for the measurement of density after being aged for at least one day at 21°C. and 50% relative humidity. Foam samples were compressed 10% on an Instron Tensile Tester, using the method of the Society of the Plastics Industry Inc. (6) except that the sample pellets had a cross-sectional area of 2.07 sq. in.

Results and Discussion

Polyols. In Table I are listed the properties of foams prepared from some castor-based polyols and the standard prepolymer. Castor oil itself produced very poor foams in this formulation so only polyols with a higher concentration of cross-linking sites (hydroxyl groups) were included. The only acceptable foam in this group was obtained from N,N-*bis*(2-hydroxyethyl)ricinoleamide.

TABLE I

Properties of Foams from Castor-Based Polyols and Standard Prepolymer

Castor-based polyol	Isocyanate equivalent	Density lbs./ft.^{3}	Comp. strength (lbs./in.^{2}) Observed	(Calcd.[a] at dens.=2.0 lbs./ft.^{3})
Hydroxylated castor oil	191	3.25	33.5	15.6
N,N-*bis*(2-hydroxyethyl)-ricinoleamide	130	2.76	45.0	27.1
Glycerol monoricinoleate	155	>9.00[b]	......	......
Pentaerythritol monoricinoletae	151	3.14	39.4	19.3
Sorbitol monoricinoleate[c]	103	3.31	42.7	19.3

[a] Calculation will be discussed later in this paper.
[b] Severe shrinkage occurred.
[c] Difficult to mix with prepolymer because of very high viscosity.

Superior foams were obtained when the standard prepolymer was reacted with a mixture of a castor-based polyol and certain more highly functional or lower-equivalent-weight polyols. These mixed polyols with lower-average-equivalent weights yielded more highly cross-linked polymers. In Figures 1–3 are illustrated the properties of foams prepared from the standard prepolymer and mixtures of three castor-based polyols with two lower-molecular-weight polyols, trimethylolpropane (TMP) and N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine (Quadrol). Polyol mixtures with average equivalent weights of 90 to 154 were used. In general, there was a decrease in shrinkage as the average polyol equivalent weight was decreased. Negligible shrinkage was observed when the polyol had an equivalent weight of 100 or less. It will be noted from the figures that there was generally a marked increase in compressive strength as the polyol equivalent weight decreased. In some cases the compressive strength appeared to go through a maximum at an average polyol equivalent weight of 100. The highest compressive strengths were obtained when mixtures of a castor-based polyol and Quadrol were used. More complete foam properties for each polyol mixture at an average equivalent weight of 100 are listed in Table II.

TABLE II

Properties of Foams from Mixtures of Castor-Based and Lower-Molecular-Weight Polyols

Polyol composition (Av. equiv. wt.=100)	Density lbs./ft.^{3}	Comp. strength (lbs./in.^{2}) Observed	Calcd. at dens.= 2.0	Percentage of closed cells[a]
Glycerol monoricinoleate				
78.0% " + 22.0% TMP[b]	2.72	52.9	32.6	
51.5% " + 48.5% Quadrol	2.33	56.6	44.5	96
Pentaerythritol monoricinoleate				
77.8% " + 22.2% TMP	2.16	42.9	38.0	93
51.2% " + 48.8% Quadrol	2.32	51.1	40.4	
Bis(2-hydroxyethyl)ricinoleamide)				
84.3% " + 15.7% TMP	2.28	49.7	40.2	....
61.5% " + 38.5% Quadrol	2.22	53.2	45.1	

[a] Determined by an air displacement method.
[b] TMP precipitates from this solution on standing over-night at room temperature.

Prepolymers. Before a standard prepolymer was chosen for this work, the utility of several prepolymers was investigated. In Table III are listed the properties of these prepolymers and foams prepared by reacting them with a polyol mixture with an average equivalent weight of 100, composed of approximately equal weights of glycerol monoricinoleate and Quadrol. The prepolymers were prepared by mixing the components for 1 hr. at 75°C. under nitrogen. The last prepolymer listed in Table III was chosen as the standard prepolymer for this investigation since it yielded foams with the best properties.

Prepolymers, similar to the standard prepolymer, were prepared from equal weights of pentaerythritol monoricinoleate and trimethylolpropane plus sufficient toluenediisocyanate to yield products with free isocyanate contents of 30% and 34%. The properties of foams prepared from these prepolymers were not sig-

TABLE III

Properties of Prepolymers and Foams Prepared by Reacting Them with 1:1 Mixture of Glycerol Monoricinoleate and Quadrol

Prepolymer (26% NCO) Composition of prepolymer	Viscosity at 25°C. cps.	Foam density lbs./ft.^{3}	Comp. strength (calcd. at dens.=2.0) lbs./in.^{2}
29.6% glycerol monoricinoleate + 70.4% TDI	1,200	2.85	24.1
30.4% pentaerythritol monoricinoleate + 69.6% TDI	2,760	2.77	24.4
30.6% glycerol mono-12-hydroxystearate + 69.4% TDI	9,840	2.68	29.7
16.6% pentaerythritol monoricinoleate + 6.6% TMP + 76.8% TDI	26,200	2.58	33.4
10.3% pentaerythritol monoricinoleate + 10.3% TMP + 79.4% TDI	90,100	2.33	38.2

nificantly different from those of foams prepared from the standard prepolymer except that, as the isocyanate content of the prepolymer increased, the foam cell structure became more coarse. Also the foam time decreased from 55 seconds to 30 seconds as the NCO content was increased from 26 to 34%.

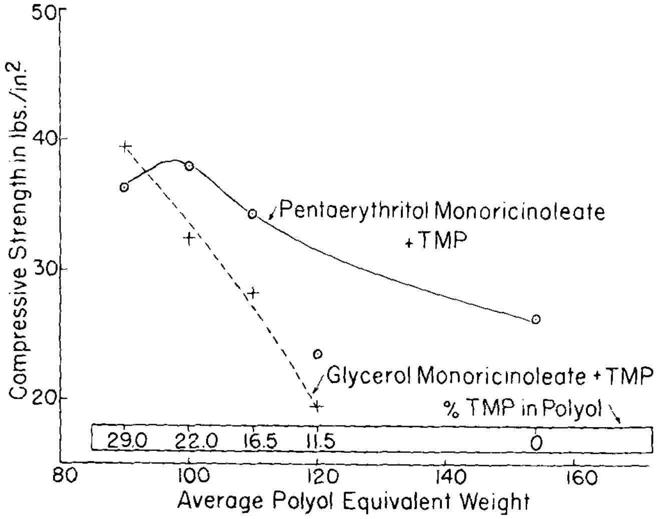

FIG. 1. Effect of proportion of TMP in polyol and average polyol equivalent weight on compressive strength (calculated to 2 lbs./ft.^{3} density), using standard prepolymer and glycerol monoricinoleate or pentaerythritol monoricinoleate.

Trichlorofluoromethane Content. A series of foams was prepared from the standard prepolymer and a polyol mixture (1:1 glycerol monoricinoleate-Quadrol) in which the concentration of trichlorofluoromethane blowing agent was varied from 11 to 29 parts/100 parts polymer. As illustrated in Figure 4, compressive strength and density decreased with increasing CCl_3F content. Also cell size and shrinkage increased as the CCl_3F content increased.

Calculation of Compressive Strength on Constant-Density Basis. Since compressive strengths varied markedly with density and since experimental foams could not always be prepared with a predetermined density, an empirical relationship between density and compressive strength in a given foam system was derived so that all foams could be compared on a constant-density basis. It was assumed that compressive strength (s) was proportional to density (d) raised to some power (n).

$$s = C\,d^n$$

The logarithmic form of this equation is:

$$\log s = \log C + n \log d$$

From this equation a plot of log s *versus* log d should be a straight line with a slope of n. The densities and compressive strengths of the foams prepared with varying CCl_3F contents are plotted in this form in Figure 5. It will be observed that the plot is approxi-

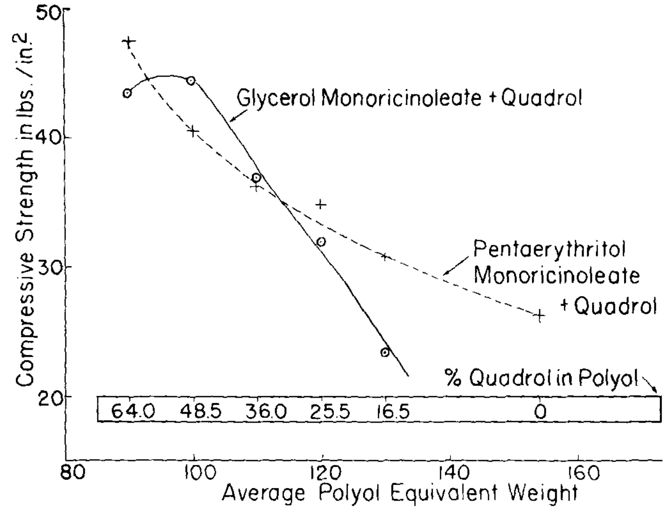

FIG. 2. Effect of proportion of Quadrol in polyol and average polyol equivalent weight on compressive strength (calculated to 2 lbs./ft.^{3} density), using standard prepolymer and glycerol monoricinoleate or pentaerythritol monoricinoleate.

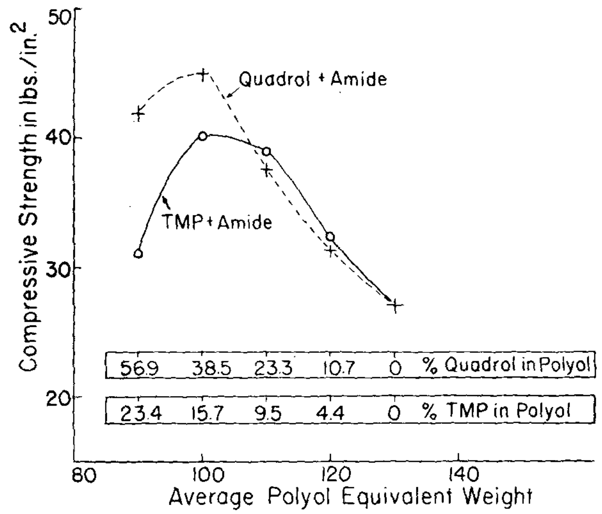

FIG. 3. Effect of proportion of Quadrol or TMP on compressive strength (calculated to 2 lbs./ft.^{3} density) of N,N-*bis*(2-hydroxyethyl)ricinoleamide urethane foams, using standard prepolymer.

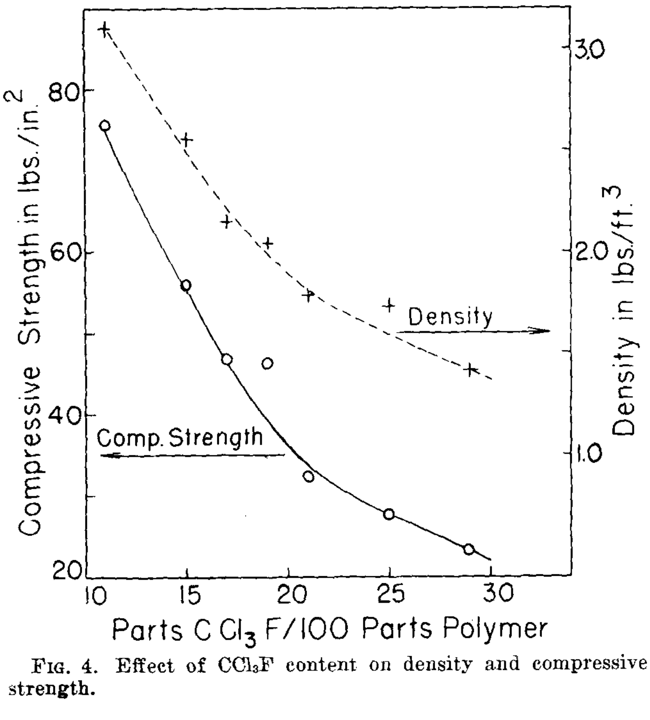

FIG. 4. Effect of CCl_3F content on density and compressive strength.

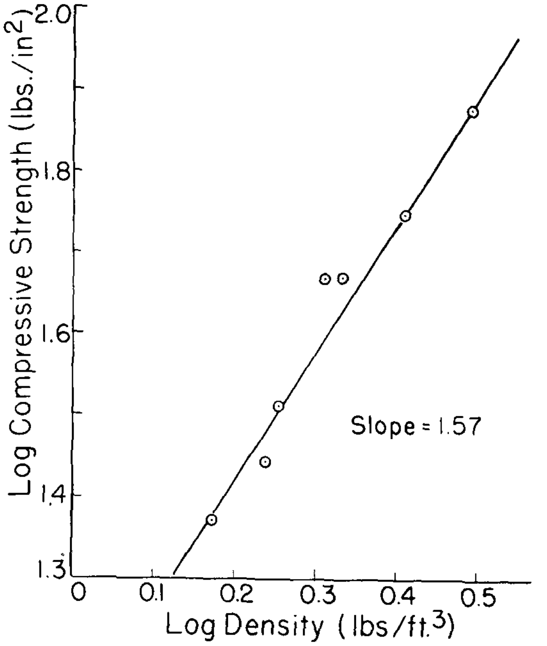

Fig. 5. Log compressive strength *vs.* log density for foams prepared with different CCl_3F content.

mately linear with a slope of 1.57. The original equation therefore becomes:

$$s = C\,d^{1.57}$$

This relationship, expressed in the following more convenient form, was used to calculate the compressive strengths at a density of 2 lbs./ft.³ of all the foams prepared in this investigation.

$$S_{(dens.=2)} = S_{observed}\,(2/d_{observed})^{1.57}$$

Catalyst. Two catalysts for the polymer-forming reaction of polyisocyanates with polyols were investigated. In Figure 6 can be seen the effect on foam time of the concentration of the catalysts Dabco and stannous octoate. The latter, the most active catalyst, was used in conjunction with (0.6 parts/100 parts of polymer) triethylamine, a known synergist. These foams were prepared from the standard prepolymer and a 77.8% pentaerythritol monoricinoleate plus 22.2% trimethylolpropane polyol mixture (Eq. wt.= 100). Dabco was the catalyst generally used in this investigation. A concentration of 0.6 parts/100 parts of polymer was chosen because this afforded a convenient foam time of about 55 seconds.

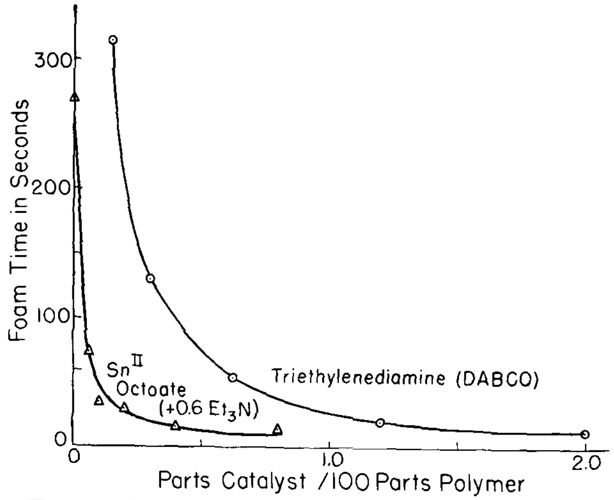

Fig. 6. Effect of catalyst concentration on foam time.

Silicone Surfactant. To obtain uniform, fine-celled urethane foams it is generally necessary to incorporate a small amount of a surfactant, usually a silicone oil. It was found that the compressive strengths of these foams were also affected by the silicone (Union Carbide, L-520) concentration, As can be seen in Figure 7, compressive strengths increased markedly with silicone content, reaching a maximum at a silicone concentration of about 1.5 parts/100 parts polymer. These foams were prepared from the standard prepolymer and polyol mixtures (Equiv. wt. = 100) of either glycerol monoricinoleate and Quadrol or pentaerythritol monoricinoleate and trimethylolpropane.

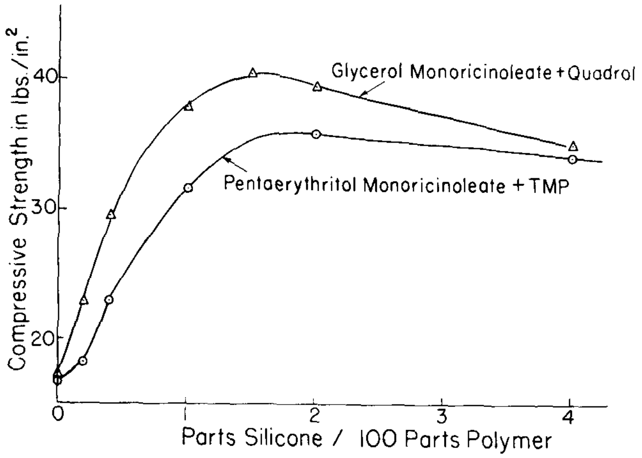

Fig. 7. Effect of concentration of L-520 silicone on compressive strength (calculated to 2 lbs./ft.³ density).

Effect of Trace Contaminants. Since the presence of a small amount of surfactant was required to obtain good uniform foams, it is not surprising that the presence of contaminants which might interfere with the action of the surfactant could have a deleterious effect on foam cell structure. Small amounts (<0.5%) of the following possible contaminants were found to cause the formation of poor, nonuniform-celled foams: wax lining from cups initially used for mixing of foam components, and lubricants (silicone grease, Lubriseal stopcock grease) used on equipment for preparation of foaming intermediates. Celvacene[3] stopcock grease was used as a lubricant when necessary since traces of this material did not affect foam cell structure.

Conclusions

Strong, low-density, rigid, solvent-blown urethane foams can be prepared from castor-based polyols and toluenediisocyanate. These foams have properties comparable to those of the best commercially-available urethane foams prepared from noncastor polyols.

Acknowledgment

The authors wish to acknowledge the assistance of T.H. Applewhite for the preparation of N,N-*bis*(2-hydroxyethyl)ricinoleamide, of R.A. O'Connell for assistance with the Instron Tensile Tester, and The Baker Castor Oil Company for generously supplying samples of castor oil products.

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[3] Consolidated Electrodynamics Corp.

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• *Letter to the Editor*

A Simple Graph for Rapid Calculation of Refining Settlement Cup

A SIMPLE, quick way to determine which of two or three refining-cup results is the settlement cup as outlined in the National Cottonseed Products Association Rule No. 201 is described in Figures 1 and 2. These charts may be of help to persons who refine cottonseed oils in laboratories throughout the country and are often faced with the annoying problem of actually having to stop and calculate every refining analysis in order to be certain they choose the correct settlement cup.

The charts are good only for cottonseed oil, using a 9.0% loss and 7.6% Lovibond Red color as the bases. They cover a wide-enough range to take care of most situations for, facetiously speaking, if your problems are losses in excess of 15% and colors that are in excess of 20% Lovibond Red, then you have problems of such a nature that charts will not help you to solve.

The charts are designed so that the color lines are approximately 10 small lines apart horizontally. This makes for easy estimation of the Lovibond Red color to the nearest 0.1 unit. If this were not true, the chart would be of little value as anything other than unity would be confusing.

In so doing, the point system at the bottom of the charts is on a rather unconventional scale, but workable, if actual premium or discount points are desired. Each small division is equivalent to 4.5 points. The actual value of these points is 4.3 points per line if perfect unity is to exist between color lines, providing the refining loss figures on the ordinate are not changed. But, as can easily be seen, if the exact point value were used, it would be very difficult to determine actual points of premium or discount by using a scale of 4.3 points per chart unit. Only once in every 10 lines would you arrive at an integer.

Therefore the system presented is the one for which it is believed that the best compromise exists or one in which unity is shown for both the refining loss and the color, and a fairly readable scale for actual premium or discount points. The color lines on the chart are exact. The 0.1 unit of color may be estimated very closely, using the "one small line equals 0.1 unit color" rule. It is really so close as to offer no serious objection because only the nearest 4.5 points can be ascertained with complete accuracy anyway.

Two charts are necessary if the wide range of losses and colors is to be covered. One chart will serve for any loss from 1 to 8% and any color from 7.6 to 20.0 Lovibond Red (Figure 1). The other chart will serve for losses from 8 to 15% and colors from 7.6 to 20.0 Lovibond Red (Figure 2).

To use the charts, enter from the left along the ordinate with the refining loss figure (one tenth % loss = 2 small lines) and proceed horizontally until the Lovibond Red color of that refining cup is reached. Drop down vertically, and read the premium or discount points on the abscissa. For convenience, the charts are designed for reading at the top and right side as well as at the bottom and left side. This reduces errors made in following horizontal lines over long distances. If the charts are entered from the left, the refining loss-color combination travelling the

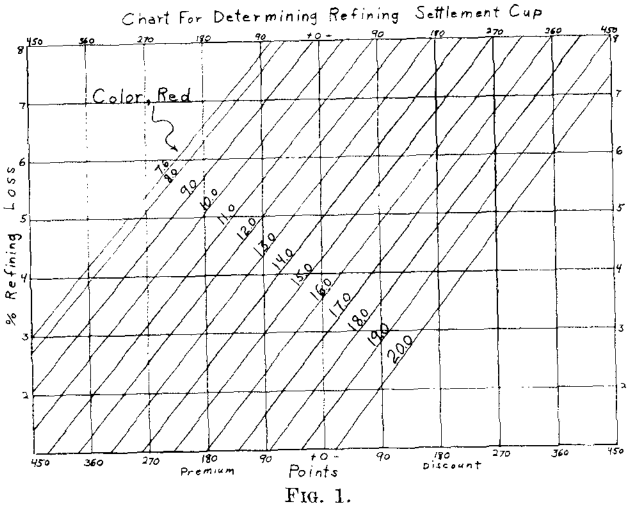

FIG. 1.

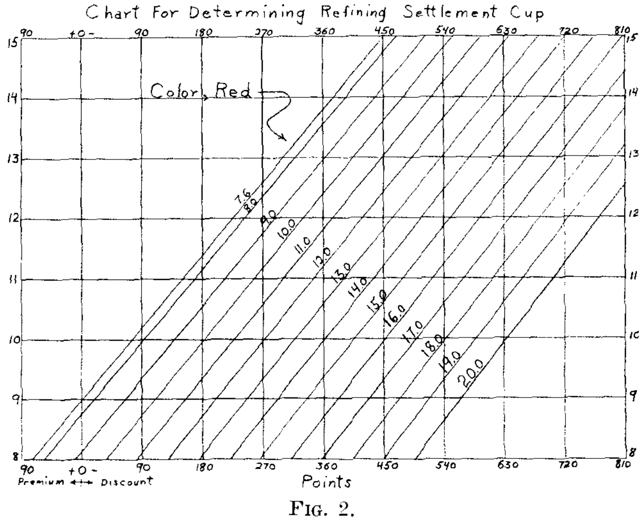

FIG. 2.