TABLE I

Functional Improvements of Dough Strengtheners in Bread

Compound	Loaf volume	Firming inhibition	Relative bread quality
Polysorbate 60	Very good	Little effect	Good
Calcium stearoyl-2-lactylate	Very good	Good +	Very good
Lactylic stearate	Good +	Good +	Very good
Sodium stearyl fumarate	Fair	Very good	Good
Sodium stearoyl-2-lactylate	Very good	Very good	Very good
Succinylated monoglyceride	Very good	Good +	Very good
Ethoxylated mono- and diglycerides	Very good	Little effect	Fair

these products are manufactured by the reaction of fatty acids with the appropriate polyol using standard esterification techniques.

Generally, at least two and as many as five of the emulsifiers are used in various combinations to give the desired functional properties. The function of surfactants in these nonbread bakery products is principally to completely emulsify the fat with the water to give a system of optimum stability. Air entrapment is also an important function in whipped products and in chemically leavened systems such as cakes and doughnuts. In these systems, entrapped air in the fat serves as foci for gas expansion. Greater quantities of finely divided fat globules containing entrapped air lead to improved volume response on baking. Tenderness and grain structure are also enhanced.

REFERENCES AND BIBLIOGRAPHY

General Background

Tenney, R.J., Baker's Dig. August 1978, pp. 24-27.

Knightly, W.H., and M.J. Lynch, Ibid. February 1966, pp. 28-31.

Birnbaum, H., Ibid. June 1977, pp. 16-24.

Mono- and Diglycerides

Feuge, R.O., and A.E. Bailey, Oil Soap 23:259 (1946).

Pyler, E.J., "Baking Science and Technology," Siebel Publishing Co., 1973, pp. 469-472.

Ethoxylated Monoglycerides

Egan, R.E., and S.B. Lampson, (to Ashland Oil and Refining Co.), U.S. Patent 3,433,645, March 18, 1969.

Egan, R.E., S.B. Lampson, and I.A. MacDonald, (to Ashland Oil and Refining Co.), U.S. Patent 3,490,918, January 20, 1970.

Moncrieff, J., and A.G. Oszlanyi, Baker's Dig. August 1970, pp. 44-46.

MacDonald, I.A., "Functionality of Ethoxylated Mono- and Diglycerides in Yeast Raised Bakery Products," Paper No. 45, 54th Annual Meeting, American Association Cereal Chemists, (1969) Abstracted in Baker's Dig. 43(3):75 (1969).

Succinylated Monoglycerides

Freund, E.H., (to National Dairy Products Corporation), U.S. Patent 3,293,272, December 20, 1966.

Meisner, D., Baker's Dig. June 1969, pp. 38-41.

Meisner, D.F., K. Lorenz, and J.L. Jonas, Cereal Sci. Today, September 1967, pp. 400-405.

Neu, G.D., and W.J. Simcox, Cereal Foods World, April 1975, pp. 203-208.

Acyl Lactylates

Thompson, J.B., and B.D. Buddemeyer, (to C.J. Patterson Co.), U.S. Patent 2,733,252, January 31, 1956.

Thompson, J.B., and D.B. Buddemeyer, (to C.J. Patterson Co.), U.S. Patent 2,789,992, April 23, 1957.

Tenney, R.J., (to C.J. Patterson Co.), U.S. Patent 3,870,799, March 11, 1975.

Del Vecchio, A.J., and J.L. Van Haften, "Physical and Chemical Properties of the Acyl Lactylates," Presented at the 66th Annual Meeting of the American Oil Chemists' Society, 1975.

Diacetyl Tartaric Acid Esters

Birnbaum, H., (to Star Kist Foods, Inc.), U.S. Patent 3,433,965, May 13, 1969.

Krog, N., JAOCS 54:124 (1977).

Polysorbate 60

Langhans, R.K., Baker's Dig. 5:54 (1971).

Sodium Stearyl Fumarate

Thomas, P.D., (to Charles Pfizer and Co.), U.S. Patent 3,343,964, September 26, 1967.

Polyglycerol Esters

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ABSTRACT

When glycerol is heated with an alkaline catalyst to over 230 C, water is evolved and polymerization occurs to form a whole family of polyglycerols ranging from diglycerol with 3 hydroxy groups, to triacontaglycerol with 32 hydroxy groups. The carboxylic acid esters of polyglycerols prepared by direct esterification or by interchange, may be solid or liquid; saturated or unsaturated; aliphatic or aromatic; mono, di- or polycarboxylic acid esters; mono-, di-, or polyesters of the polyglycerol; single or mixed acid esters; high or low molecular weight; water or oil soluble; and with an HLB from about 4 to about 13. Polyglycerol esters find utility in a wide variety of food products including beverages, desserts, toppings and baked goods. They are thermally stable and find application in several industrial systems.

Polyglycerol esters have been commercially available for about 20 years. At the present time, they are being offered by at least six companies in the United States and several others in Europe. Several food products list polyglycerol esters on their ingredients labels. In spite of the general availability and frequent use of these compounds, many people utilizing emulsifiers are barely aware of their existence or of their broad functionality. The purpose of this paper is to describe the general methods of manufacture as well as some of the properties and uses of polyglycerols and their fatty esters.

Polyglycerols are most often prepared by the polymerization of glycerol under alkaline conditions at elevated temperatures (1). The condensation reaction (Fig. 1) involves the α-hydroxyl groups of two glycerol molecules which react to form an ether linkage with the consequent expulsion of a water molecule. The two α-hydroxyl groups remaining on the diglycerol molecule thus formed are available for reaction with other molecules of glycerol or other polymerized molecules. The reaction produces polymers which apparently are almost entirely linear (2). Care must be taken during the polymerization reaction to exclude air from the system. Traces of oxygen lead to the formation of acrolein as well as a dark product which is not easily bleached.

It is advisable to follow the reaction rate or degree of polymerization by determination of viscosity, refractive index, or hydroxyl value. The hydroxyl value is usually the best indicator of the amount of polymerization which has occurred. When the average molecular weight of the polymer has reached a predetermined value, the reaction is terminated by cooling and acidulation. When required, the polyglycerol may be bleached with special activated carbons, clays, ion exchange or chemical agents (3,4). If the acrolein content of the polyol is high, it may be necessary to steam strip the product under vacuum before the bleaching step.

The polymerization reaction proceeds by chance, and the molecular size distribution would be expected to follow a normal distribution pattern. As a result, the commercial product does not contain a pure molecular specie but a mixture of similar molecules having the average molecular weight of the name polyol. The most frequently manufactured polyglycerols are diglycerol, triglycerol, hexaglycerol, octaglycerol and decaglycerol. Although higher polymers may be easily prepared, they are seldom manufactured, since they are not permitted for use in foodstuffs.

The polyglycerols are dense, viscous liquids and are difficult to handle at ordinary temperatures when water-free. Typical densities and viscosities of some commercially prepared polyglycerols are shown in Table I. When selecting equipment for the manufacture and handling of these polyols and their esters, the effects of both viscosity and density must be taken into consideration.

Esters are most simply made by direct esterification of the polyol with a free organic acid. The reaction proceeds smoothly at elevated temperatures; the only byproduct of the reaction is water, which is immediately volatilized. These compounds also can be made by the intermolecular arrangement of a triglyceride with a polyol in the presence of a suitable alkaline catalyst. When this method is used, the glycerol can either be continuously removed under vacuum or left as part of the reaction mixture in the form of mono-and diglycerides. In either case, the reaction must be carried out under an inert atmosphere to obtain good color, flavor and odor characteristics. Equipment used must be designed to heat quickly to temperatures above 200 C and to agitate the system well.

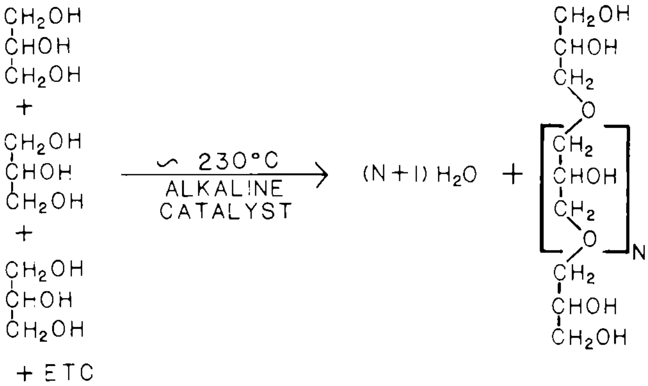

FIG. 1. Preparation of polyglycerols.

The treatment given the reaction mass after the esterification or transesterification is usually dependent on the degree of esterification. When about one-third or less of the hydroxyl groups are esterified, the reaction mixture is neutralized and cooled to around 90 C or slightly higher. The unagitated mass is held at this temperature to allow free polyols to settle. The free alcohols are then separated, the product is filtered and it is then packaged. Normal bleaching procedures are not useful with these products.

When complete or nearly complete esters are prepared, no settling period is required. Moreover, the products can be treated much the same as triglycerides. They can be bleached and deodorized by the usual procedures employed with fats and oils.

A large number of ester compounds may be synthesized from a given polyol. For example, it is technically possible to prepare 12 different esters from the reaction of only decaglycerol and oleic acid by varying the stoichiometric quantities of the two ingredients. This excludes consideration of positional isomers which can be formed. Theoretically, it is possible to form six different decaglycerol monooleates and thirty-six decaglycerol dioleates when all positional isomers are considered.

In the commercial manufacture of partial esters, the reaction proceeds according to chance. In a homogeneous system the esterification reaction gives a mixture in which the fatty acid radicals are distributed at random among all available hydroxyl groups. The composition of the product can be calculated. For the reaction of one, two and four moles of stearic acid with one mole of polyol (Fig. 2), compounds present at less than 0.1% were disregarded (5). Unless otherwise noted, the compositions given in the following discussions are all weight percentages. The polyols are assumed to be pure compounds to simplify the calculations.

When equimolar quantities of triglycerol and stearic acid are reacted, nearly one-third of the triglycerol does not react with the acid; the equilibrium reaction mass contains slightly over 15% free polyol. The monostearate and distearate represent 41 and 31%, respectively, of the mass composition. If calculated on a triglycerol-free basis, the respective values are 49 and 47%. When the molar ratio of stearic acid to triglycerol is increased to 2:1, the diester is the predominant specie (35 weight %). The free polyol content has fallen to 2.4%. The tristearate content has risen to 32%, and a small amount of the complete (penta-) ester is present.

TABLE I

Typical Viscosities and Specific Gravities of Commercially Prepared Polyglycerols

Polyglycerol	Specific gravity	Viscosity, cs. 65.6°	Viscosity, cs. 99 C
Triglycerol	1.279	640	70
Hexaglycerol	1.283	1700	110
Decaglycerol	1.290	3200	280

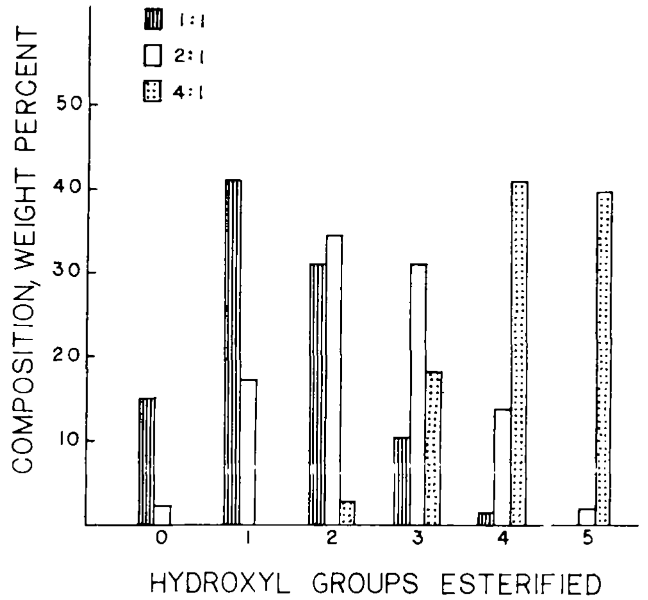

FIG. 2. Composition at equilibrium of single-phase reaction mixtures of triglycerol and 1, 2 and 4 mole equivalents of stearic acid.

The reaction of four moles of stearic acid with one mole of triglycerol will esterify 80% of the hydroxyl groups. The tetra- and penta- esters account for ca. 80% of the product weight. The di- content is only 3%.

As shown in Figure 3, the reaction of stearic acid with hexaglycerol is somewhat similar to that of triglycerol, but it must be kept in mind that hexaglycerol has eight hydroxyl groups whereas triglycerol has but five.

Decaglycerol, with twelve hydroxyl groups available for reaction, produces ca. 38% by weight of the monoester when combined with an equimolar quantity of stearic acid (Fig. 4). The free polyol content of the reaction mixture is 26%. The di-stearate ester is present at the 24% level. As the molar ratio of stearic acid to polyol is increased, the free alcohol content is diminished rapidly. The number of molecular entities is increased markedly. At the 4:1 ratio, eight compounds are present at levels over 2%. When the ratio is increased to 6:1 (data not shown) the shape of the distribution curve is similar to that at the 4:1 ratio but is slightly flattened. This exercise indicates that commercial preparations of partial esters of polyglycerols are normally mixtures of several related compounds. Moreover, mono- and diesters may contain significant amounts of free polyol unless steps are taken for removal.

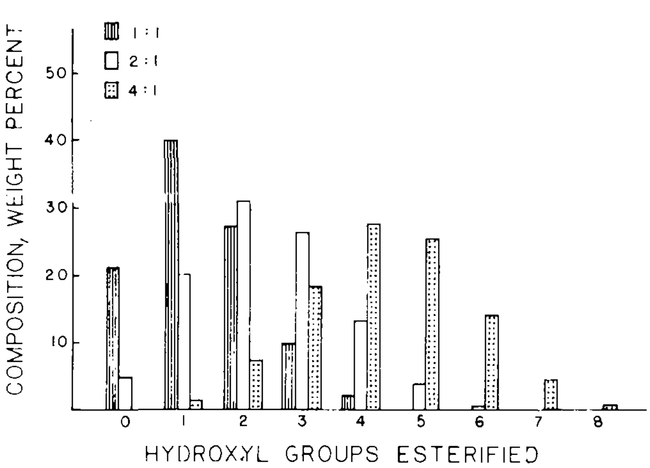

FIG. 3. Composition at equilibrium of single-phase reaction mixtures of hexaglycerol and 1, 2 and 4 mole equivalents of stearic acid.

The hydrophilic-lipophilic properties of polyglycerol esters are controlled by the size of the polyglycerol moiety, the chain length of the esterified fatty acid, the degree of unsaturation of the fatty acid, the number of hydroxyl groups which remain free after esterification, and the presence of other compounds in the product. The changes in properties due to these factors will be noted later.

The utility of most polyglycerol esters is dependent upon their hydrophilic-lipophilic properties; in other words, the HLB range covered by these unique esters. In all the discussions which follow, HLB values were calculated by the Griffin formula:

$$HLB = 20\,(1\text{-}S/A)$$

where S is the saponification value of the ester, and A is the acid value of the fatty acid used in the ester preparation. The higher the HLB value the greater its hydrophilic property. The HLB scale covers values in the range from zero to twenty. Although empirical, this simple method is widely used by formulators of emulsified systems.

The range of HLB values of compounds which are theoretically possible to obtain by esterifying triglycerol with organic acids is shown in Figure 5. In this graphic representation it is noted that variations in HLB of triglycerol esters occur when the molecular weight of the esterified fatty acid is changed. The number over the horizontal line represents the degree of esterification; i.e., the number of molecules of the straight chain organic acid combined with a molecule of triglycerol. Two conclusions are easily drawn. A decrease in the molecular weight of the fatty acid or portion of the molecule results in an increase in the hydrophilic nature of the ester. The monoesters range in HLB value from 15.7 for the monoacetate to 8.8 for the monostearate. An increase in the number of fatty acid moieties reacted with the polyol molecule (with a corresponding decrease in the number of free hydroxyl groups) will result in a more lipophilic product. For example, the HLB values for triglycerol stearate esters range from 1.9 for the pentastearate to 8.8 for the monostearate; the corresponding palmitate esters range from 2.1 to 9.3.

As shown in Figure 6, the decaglycerol esters offer a much greater range of hydrophilic-lipophilic properties than the triglycerol esters. The twelve hydroxyl groups of decaglycerol offer a much greater opportunity to develop the higher HLB esters than those polyols with fewer hydroxyls. Note that the HLB values for the monoesters range from over 18 for the monoacetate to ca. 14.5 for the monostearate. These values are 3 and 5 HLB units higher than the corresponding monoesters prepared from triglycerol.

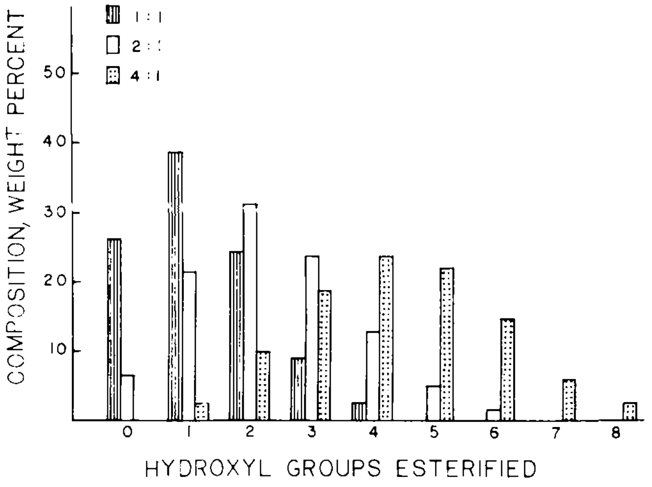

FIG. 4. Composition at equilibrium of single-phase reaction mixtures of decaglycerol and 1, 2 and 4 mole equivalents of stearic acid.

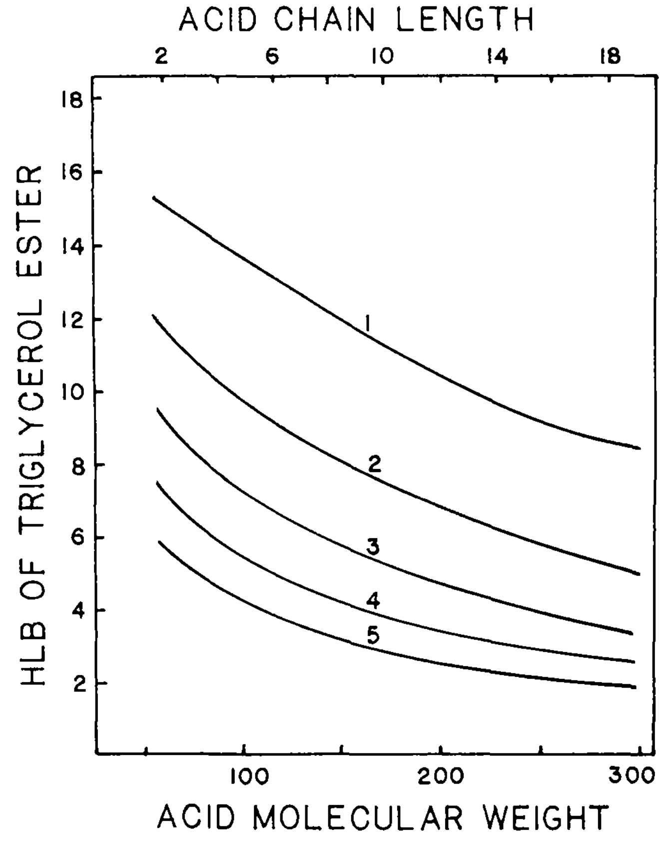

FIG. 5. Effect of fatty acid chain length and degree of esterification on the HLB of triglycerol esters.

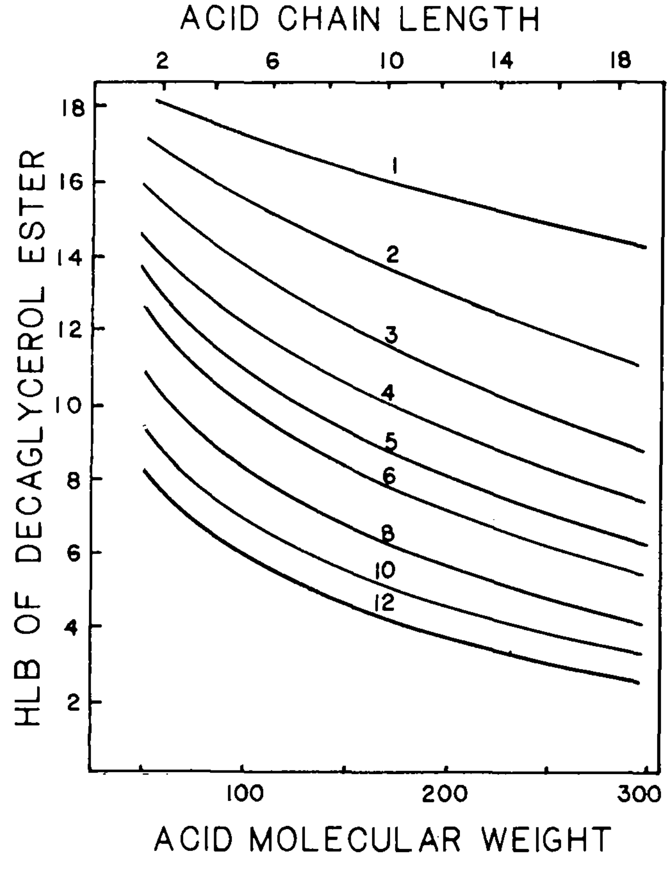

FIG. 6. Effect of fatty acid chain length and degree of esterification on the HLB of decaglycerol esters.

The differences in the HLB ranges covered by the stearate esters of tri-, hexa- and decaglycerols is indicated in Figure 7. This shows that a decrease in the free hydroxyl content lowers the HLB, the esters of decaglycerol cover a wider range than those of triglycerol and hexaglycerol and the HLB range from about 3 to 8 can be covered by esters of all three polyols. In commercial preparations, the HLBs of polyglycerol monoesters are not as high as expected unless we take into consideration the laws of random distribution during the esterification. As just noted, calculated values for the pure stearic acid monoesters of tri-, hexa- and decaglycerols are 8.8, 12.2 and 14.5. We find that the calculated HLB of the esters obtained from reaction of equimolar quantities of stearic acid and the polyols is 6.7, 10.1 and 12.5 (on a polyol-free basis). The lower values are due to the presence of significant quantities of the di- and tri-esters. In other words, in order to approach the theoretical HLB values for the monoesters, large excesses of polyol would be required. To make this economically feasible, the free polyol must be separated from the ester inexpensively and then recycled.

Table II shows the calculated HLB values for the stearate esters shown in Figures 3-5. The values in parentheses indicate theoretical values for the pure mono-, di-, tetra-esters. In these computations, all products are free of uncombined polyol. The data show that when two moles or less of the fatty acid is reacted with a mole of polyglycerol, the HLB of the system is considerably lower than that of the corresponding pure ester. At higher ratios of fatty acid to polyol, the distribution of higher and lower substituted esters tends to balance one another; these esters have HLB values equivalent to the corresponding nonrandomized molecular entities.

Production of polyglycerol esters with low fatty acid to polyol ratios results in compositions with high free polyglycerol content. If the reaction is not carried out entirely under homogeneous conditions, then even higher amounts of free polyol will be present. Under the proper conditions, much of this unreacted component may be removed. If the

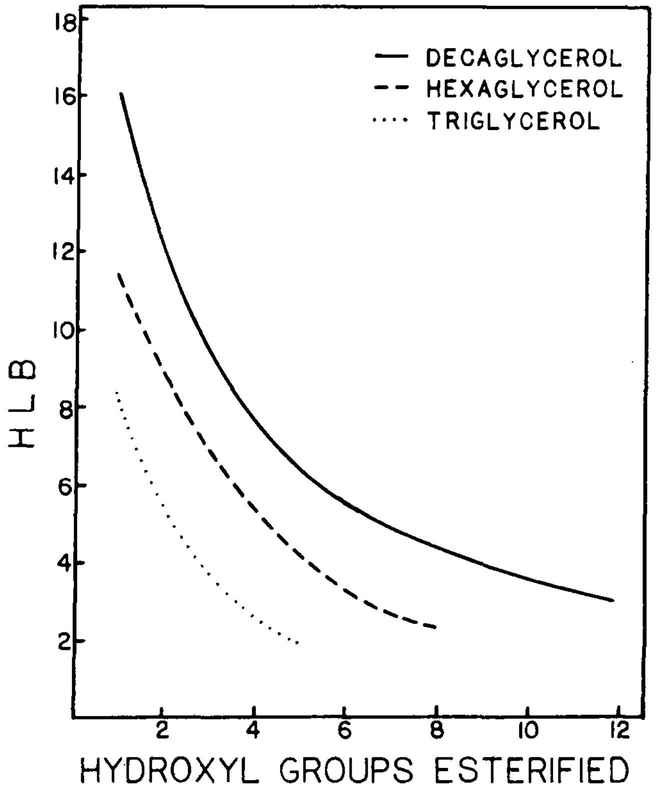

FIG. 7. HLB ranges covered by stearic acid esters of triglycerol, hexaglycerol and decaglycerol.

TABLE II

HLB Values Calculated from the Theoretical Compositions of Products Formed by Reaction of Stearic Acid with Polyglycerols

	HLB		
	Molar ratio of stearic acid/polyol		
Polyglycerol	1:1	2:1	4:1
Triglycerol	6.7 (8.8)	4.9 (5.3)	2.6 (2.6)
Hexaglycerol	10.1 (12.2)	8.1 (8.8)	5.1 (5.1)
Decaglycerol	12.5 (14.5)	10.6 (11.2)	7.5 (7.5)

free polyol content is low, the saponification value of the product can be an important determination. With any given fatty acid, the Griffin HLB calculation can be shown to follow the formula for a straight line, $y = mx + b$; where y is the HLB and x is the saponification value of the ester. In other words, the HLB is directly related to the saponification value of the ester. With the decaglycerol oleates and stearates, a change in the saponification value of ten (the units are mg of KOH per g) will result in an HLB difference of one. For this reason, specifications for these esters should contain reasonable restrictions on the saponification value if the HLB is critical in the end use. If the preparation contains significant quantities of free polyol, the saponification value itself is not sufficient to describe the nature of the ester.

Data published earlier indicate that the decaglycerol mono-, diesters of capric acid, or acids containing fewer cabon atoms, are water soluble (6). In order to prepare high HLB fatty esters from polyglycerols, one must either use the shorter chain fatty acids, such as those derived from coconut oil, prepare the longer chain acid esters from glycerol polymers greater than decaglycerol, or use large excesses of polyol in the preparation.

When we consider only those esters permitted for use in foods, the number of compounds which can be manufactured is greatly reduced. At the present time, polyglycerol esters derived from palmitic, stearic, oleic, and linoleic acids, or oils containing these acids, are acceptable for food use. Polyglycerols having an average of ten or less glyceryl units per molecule can be used in edible preparations; higher polymers are not permitted at this time (7). The HLB range which can be practically covered by esters of stearic, oleic and linoleic acid is about three to thirteen. When palmitic acid is used in the esterification the range can be extended to about 14. Since the range covered by the stearic and oleic esters is about the same, those persons using the esters in formulation work may have a choice of liquid or solid product.

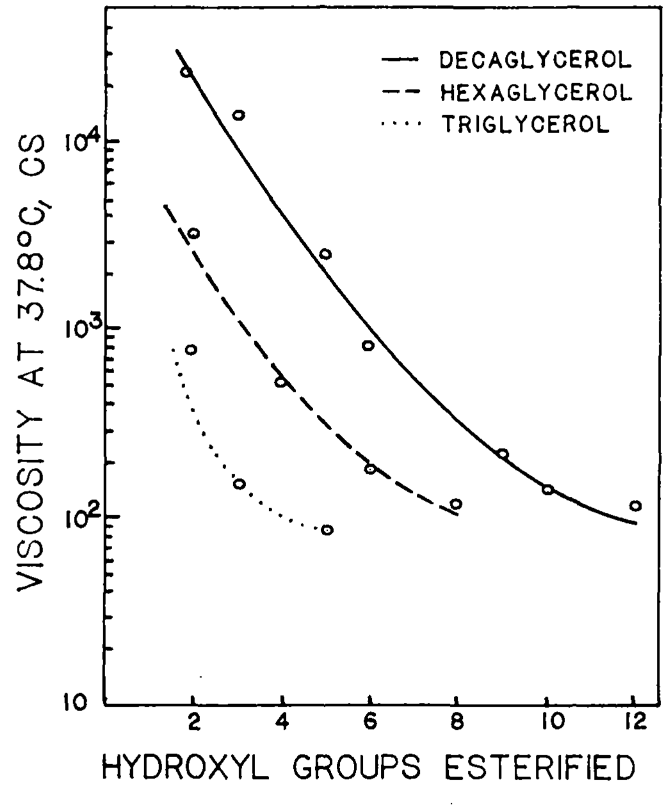

FIG. 8. Viscosity of polyglycerol esters.

The stearate esters of triglycerol, hexaglycerol and decaglycerol are all solids at room temperature. Those with saponification values of less than ca. 120 to 125 are waxy and slightly pliable: higher stearate content produces compounds which are firmer. The complete esters and those partial esters having few free hydroxyl groups, for example, triglycerol tristearate and decaglycerol octastearate, are brittle solids. The melting points of such compounds are in the 60 to 65 C range, whereas the softer products melt in the 55 to 60 C range. For this reason most polyglycerol stearates are made from a blend of stearic and palmitic acids. The melting point of an ester can be lowered as much as 8 C when the palmitate content is increased to ca. 35%. The physical appearance at room temperature is the same, but they are easier to disperse in oil or water. The HLB is slightly increased. The stearate esters are most easily handled as flakes or beads.

The oleate esters are liquids at room temperature. The viscosities of the oleates are dependent on the molecular weight of the polyglycerol moiety, the degree of esterification and the temperature of the ester. The effects of these parameters on the viscosities of polyglycerol esters are shown in Figure 8. The viscosity of the decaglycerol dioleate at 37.8 C is ca. 20,000 cs. When it is heated to ca. 65 C, the viscosity is reduced to ca. 6000 cs; it is readily pumped at temperatures above 90 C. The hexaglycerol oleates are less viscous than the corresponding decaglycerol esters; the triglycerol esters are even less viscous. These products can be handled at temperatures above 50 C.

The stearate esters, at temperatures above their melting points, exhibit viscosity properties similar to those of the corresponding oleate esters at that temperature.

At 37.8 C temperature, the specific gravities (Fig. 9) of the decaglycerol mono-, di-, tri-, tetra- and pentaoleates are greater than one; those having higher amounts of oleic acid esterified are less dense than water. Hexaglycerol oleates follow a like pattern. Those heavier than water have three or less oleic moieties per molecule. In the triglycerol series, only the monooleate is as dense as water. Mono-, dioleate mixtures offered commercially have a specific gravity of just slightly over one.

At high temperatures, polyglycerol esters have excellent thermal stabilities (Table III). At 200 C, only about a quarter of the weight of the sample was lost when exposed for 16 hr in a forced draft oven. In the presence of an efficient antioxidant, the products did not form a resin, but remained fluid throughout the test. At the higher temperatures, carbonization occurred during this time period and resinous products were formed. In another experiment, the compounds were heated 10 min on a hot plate. Losses of less than 50% were observed and the products remained liquid at 250 and 300 C.

At the present time, polyglycerol esters find acceptance in a very broad area of application. In the following discussion of usages, we do not wish to give the impression that these ingredients are the only emulsifying materials in a given system. In some cases, they do not require other agents, but often they are blended with monoglycerides,

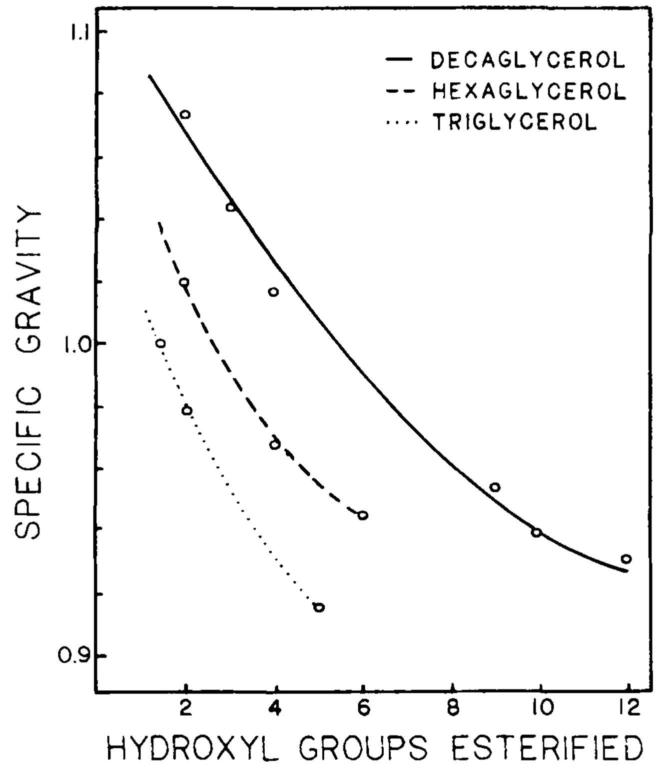

FIG. 9. Specific gravity of polyglycerol esters.

sorbitan polyoxyethylene esters or other compounds.

Polyglycerol esters have several uses in the edible oil industry. They have been employed as high quality crystallization inhibitors which do not contribute color or off-flavor to refined salad and cooking oils. The use of polyglycerol esters as antispattering agents in cooking oils has been patented. Icing shortening containing polyglycerol esters are marketed for use by bakeries and allied industries. Blends of polyglcerol esters and monoglycerides have been used in commercial high ratio cake shortenings in Europe; this use has not been developed in this country but a great potential exists.

The polyglycerol mono- and distearates are especially useful in toppings, aerated gelatin desserts and frostings where high foam stability is required. Several patents have been issued covering these types of formulation. These foods usually have a low fat content and the emulsifier contributes to their texture and pleasing mouth character. Low fat imitation ice creams also depend on the same type of emulsifier to give them their unique properties. The polyglycerol esters also have caloric values between those of fats and carbohydrates; this is important in the formulation of low caloric foods. In the confectionery industry, their use has been suggested as agents to bond sugar and fat, anti-bloom agents, and compounds which control viscosity of coatings. This area of use has not been fully investigated at this time.

TABLE III

Heat Stability of Polyglycerol Esters

Compound	Weight loss[a] at		
	200 C	250 C	300 C
Triglycerol			
mono, dioleate	26	78	89
pentaoleate	25	71	78
Hexaglycerol			
dioleate	26	76	80
distearate	25	86	91
Decaglycerol			
tetraoleate	20	67	74
dodecaoleate	27	55	57

[a] 0.2 g in a 60 mm aluminum foil dish for 16 hr in a forced draft oven. Antioxidant present.

Several coffee whiteners list polyglycerol partial esters on their ingredient labels. The use of decaglycerol mono-dioleates as clouding agents for beverages including both still and carbonated beverages is well known. Manufacturers and formulators of flavors find the oleates with HLB value above six to be effective solubilizers and carriers of essential oils and essences. The pharmaceutical and cosmetic manufacturers have utilized these compounds as part of emulsifier systems, thickening agents and opacifiers. Polyglycerol oleates have been tested as therapeutic agents, and interest has been shown for their use as replacements for bile salts in some malabsorption syndromes.

In the area of fiber lubricants and finishes, polyglycerol oleates have been utilized for a number of years. The partial esters are used as part of the critical emulsifier system required to apply and/or remove lubricant from fiber surfaces. They apparently contribute to fiber-rubber adhesion when applied to tire cord and possess good antistatic properties. The high temperature stability of some esters suggests their use in texturing and related processes. Various polyglycerol esters have been marketed for nearly two decades, but only in the last few years have widespread interests been shown in applications. This is believed due to increased competitiveness from more suppliers, greatly improved products and need for highly functional emulsifying systems. The usage of polyglycerol esters is expected to increase dramatically in the years ahead.

REFERENCES

1. Harris, B.R., U.S. Patent 2,258,892, October 14, 1941.
2. Babayan, V.K., T.G. Kaufman, H. Lehman, and R.J. Tkaczuk, J. Soc. Cos. Chem. 15:473 (1964).
3. Babayan, V.K., and H. Lehman, U.S. Patent 3,637,774, January 25, 1972.
4. Hunter, R.H., U.S. Patent 3,742,069, June 26, 1973.
5. Lewis, R., G. Halaby, and R. McIntyre, Stokely-Van Camp, Inc., unpublished data.
6. Babayan, V.K., and R.T. McIntyre, JAOCS 48:307 (1971).
7. Federal Register 21, 172.854 (1977).