Esterification and Interesterification

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ESTERIFICATION AND INTERESTERIFICATION are not at all new as industrial processes applied to fatty materials; as unit processes they have been a subject for intensive scientific study and practical invention for more than a century. Yet they continue to hold new interest for those engaged in the fatty oil industries and are being utilized apparently at an accelerating rate. New proposals are being put forward frequently for commercial applications of these processes; in view of the large tonnage of fat now being processed by methods which had hardly been operated outside a research laboratory 10 years ago, it seems safe to predict that in the next decade many more of the proposed applications will be put into practice and still other ways will be found to make better and cheaper products with the aid of these processes.

We shall not attempt in this brief discussion to describe esterification and interesterification in all their varieties and applications; it should be more instructive to concentrate upon some of the principles and relationships that seem especially interesting, illustrated by a few concrete examples of going processes. But as a preliminary, it may be well to list some of the fields in which the processes have been or may be applied (Table I).

TABLE I

Industrial Applications of Esterification and Interesterification
(Partial list of actual and proposed operations)

	Reviews
Direct esterification of acid and alcohol	1, 2, 23
Fatty acids, with monohydric alcohols, to make plasticizers, intermediates, esters for fractionation in analysis and research	
Fatty acids, with polyhydric alcohols with glycerol, to make monoglycerides with other polyols, to make emulsifiers, drying oils (4, 5, 6, 15) and other products	3
Mixtures of acids, with polyhydric alcohol oil modified alkyd resins (20) tall oil esters (21, 22)	
Rosin acids, with polyhydric alcohols ester gum and other resins (16, 17)	
Fatty alcohols, with fatty acids or other acids	24
Alcoholysis	
Triglycerides and monohydric alcohols methanol, to make methyl esters and glycerol (7) other alcohols	23
Triglycerides and glycerol, to make monoglycerides, for use in edible products (18) monoglycerides, as step in manufacture of alkyds (19)	
Triglycerides and other polyols	3
Ester-ester interchange, reaction in single phase, without removal of a product during the reaction Exchange of radicals among triglycerides of a natural fat	9, 37, 38
improved shortening from lard (8, 10, 11, 15)	
Exchange among triglycerides of fat mixtures	23
Ester-ester interchange in two-phase system, with reaction influenced by precipitation or removal of a product ("directed interesterification")	
Exchange of radicals among glycerides of a natural fat, with simultaneous crystallization	12, 13, 37, 38
improved shortening from lard (14)	

The chemistry of these processes is basically the same, regardless of the kinds of acids and esters involved, with a few exceptions, and when they are applied to fatty materials, the usual considerations apply to the operation and control of the processes, provided that due allowance is made for the effects of mutual solubilities and relative reaction rates of the various reactants. They are reversible reactions which conform reasonably well with the law of mass action when carried out in homogeneous systems, and

TABLE II

Esterification of Equivalent Quantities of
Acid and Alcohol at 155°C. (Menschutkin)

	% Conversion to Ester		Equilibrium Constant, K
	1 hr.	Limit	
Alcohols with acetic acid			
Methyl	55.59	69.59	5.24
Ethyl	46.95	66.57	3.96
Propyl	46.92	66.85	4.07
Butyl	46.85	67.30	4.24
Allyl	35.72	59.41	2.18
Dimethylcarbinol	26.53	60.52	2.35
Trimethylcarbinol	1.43	6.59	0.0049
Phenol	1.45	8.64	0.0089
Acids with isobutyl alcohol			
Formic	61.69	64.23	3.22
Acetic	44.36	67.38	4.27
Propionic	41.18	68.70	4.82
Butyric	33.25	69.52	5.20
Isobutyric	29.03	69.51	5.20
Trimethylacetic	8.28	72.65	7.06
Phenylacetic	48.82	73.87	7.99
Benzoic	8.62	72.57	7.00

accordingly the rate and extent of reaction in any given case can be influenced by the relative proportions of the reactants or by the withdrawal of a product from the sphere of action while the reaction is going on.

For esterification reactions in general, Leyes (1) has shown graphically how the proportion of alcohol to acid affects the yield of ester at equilibrium when the reaction is carried out in a homogeneous system. When the reaction is one with a very favorable equilibrium constant, $K = 10$, such as occurs for example when para-toluic acid is esterified with a typical primary alcohol, a high degree of conversion is obtained without a large excess of alcohol; with one equivalent of alcohol, the conversion would be about 76%, and with two equivalents or more, the conversion at equilibrium is better than 90%. At the other extreme, a reaction with a very small K (0.0001), such as would apply for the esterification of some tertiary alcohols with fatty acids, the conversion at equilibrium would be only about 3%, even though 10 times the equivalent quantity of alcohol were used. In such a case, it would be impractical to carry out the esterification without upsetting the equilibrium by removing one of the products, or by using some indirect method.

Different alcohols differ to a remarkable degree in their reaction rates and in their equilibrium constants for reaction with a given acid. Different acids also differ radically in their reaction rates but tend to be more nearly alike in degree of reaction at equilibrium with a given alcohol. Trimethylacetic acid, for example, reacts very slowly, no doubt because of steric effects, but if given enough time, it will react as completely, or more so, than corresponding unbranched acids. A few of these relationship are shown in Table II. Lauric and palmitic acids produce the same molar proportion of ester as do acetic and butyric acids when brought to equilibrium with isopropyl alcohol in solution in dioxane, which produces a homogeneous system in each case (26). The extreme differences that exist among various organic acids in their rates of esterification under comparable conditions have been confirmed by numerous experiments made more recently than those summarized in Table II. In a series of aliphatic acids beginning

with acetic acid, increased branching of the chain decreased the rate of acid-catalyzed esterification. With a high degree of branching the reaction was as much as 7,000 times slower than that of acetic acid, and a few extreme cases were found with a rate too slow to measure (28, 29). A few of these data are shown in Table III. These differences in rate are attributable to steric effects, and it has been pointed out that the acids having a large number of atoms in the 5 or 6 position, counting back from the oxygen of the carbonyl group as number 1, would have a great deal of hindrance (28). Comparing aromatic acids with aliphatic, benzoic acid esterifies much less rapidly than acetic acid. In view of this it is not surprising that the ortho-substituted benzoic acids with substituents in both the 2 and 6 positions are so strongly hindered that their esters can hardly be made at all by the direct esterification route.

In comparison with the effect of branching of the chain near the carboxyl group, differences in chain length of normal fatty acids have little effect on the esterification rate. It might be supposed that stearic acid, and other higher fatty acids, would be less reactive than acetic acid, but actually, except for formic acid, the different acids in the acetic acid series differ very little from each other, either in acidity or esterification rate, provided that the comparisons are made under conditions which eliminate solubility effects. Unsaturated fatty acids are said to esterify somewhat more slowly than the corresponding saturated acids (Table IV), but the difference is relatively small when the unsaturation occurs at some distance out on the chain from the carboxyl group, as it does in nearly all of the natural unsaturated fatty acids. A double bond at the 2 position, as in acrylic acid or 2-octadecenoic acid, causes the reaction to be considerably slower.

In practical esterification of natural fatty acids and fatty acid mixtures, differences in rate among the different individual acids are seldom noticed, but the same is not true for mixtures of fatty acids with other types of acids. In the case of tall oil, for ex-

ample, the rosin acids in the mixture esterify so much more slowly than the fatty acids that a considerable degree of selective esterification can be practiced (21). The practical esterification of higher fatty acids usually is essentially very simple, especially when the alcohol involved is relatively nonvolatile, as is the case with glycerol, pentaerythritol, and other alcohols often used. In these cases it is relatively easy to remove the water produced by the reaction without complicated means for preventing the loss of one of the reactants. Furthermore the temperature in most cases can be high enough to give a reasonable reaction rate without the use of catalyst, and it is simply necessary to provide sufficiently good agitation to keep the reactants well mixed, especially at the beginning when the system may consist of two phases differing considerably in density, and to provide conditions which favor the removal of moisture as rapidly as it is formed in the reaction. For this latter purpose reduced pressure or sparging with inert gas or super-heated steam or combinations of these measures are effective. In this connection it may be remarked that steam passing through hot oil in a vessel at reduced pressure is in a highly super-heated state and is an effective and economical drying-agent.

Several publications have given data on the esterification of natural fatty acid mixtures, such as peanut fatty acids with glycerol (27), linseed fatty acids with pentaerythritol and other polyols (25). Appropriate temperatures for such operations are in the range of about 190° to 240°C.

Rosin acids require higher temperatures because they have a much slower rate of esterification, attributable to steric effects of the kind that has been discussed. Comparison of typical data for fatty acids (27) with typical data for rosin (16, 17) show that a temperature at least 75°C. higher is required to make rosin esterify at a rate comparable with that of fatty acid.

In spite of the basic simplicity of the uncatalyzed esterification of fatty acid with polyhydric alcohols at high temperature, it is not easy to get a high degree of completeness of reaction if the product is to have both a low content of free hydroxyl and a low acid value. The shape of the curve for acid value (or hydroxyl value) vs. time is such that a long time may be required to reach a desired degree of completeness of reaction unless an excess of one of the reactants can be used and left in the product or removed after the completion of the esterification.

The simple high temperature esterification with removal of water by distillation may not be appropriate for some operations, as for example, those involving a volatile alcohol. In such cases other devices may be resorted to for forcing the reaction toward completion, such as the use of a catalytic reaction at lower temperatures, reaction under pressure, use of an excess of alcohol followed by removal of the excess from the product, and the use of some device for removing one of the products during the course of the reaction. For some cases the removal of water by azeotropic distillation with benzene or xylene during the reaction is very effective. This device makes it possible even to prepare the esters of fatty acids with various phenols which ordinarily were considered to be difficult or impossible to esterify by direct reaction (30). Numerous patents have described various methods

TABLE III
Acid-Catalyzed Esterification of Aliphatic Acids
(0.005 Molar HCl) (28)

Acid	$k_{H^+}^a$ X 10^3	$\dfrac{k_{H^+} \; CH_3COOH}{k_{H^+} \; RCOOH}$
CH₃COOH	44.0	1
CH₃CH₂COOH	40.0	1.19
CH₃CH₂CH₂COOH	21.1	2.02
Higher alkanoic		2.02 ave.
(CH₃)₂CHCOOH	14.7	3.00
(CH₃)₃CCOOH	1.40	26.8
(CH₃)₃CCH₂COOH	0.814	42.7
(CH₃)₃CCH(CH₃)COOH		1616
(CH₃)₃CC(CH₃)₂COOH		7765

ᵃk in liters/mole/sec.

TABLE IV
Velocity Constants for the Esterification of Various Fatty Acids
and Methyl Alcohol Catalyzed by Hydrochloric Acid [a]

Acid	k	Acid	k
Formic	2568	Lauric	121.9
Acetic	239	Myristic	120.9
Propionic	211.7	Palmitic	114.4
Butyric	115.2	Stearic	123.7
Valeric	123.2	Undecenoic	53.0
Caproic	118.7	Oleic	54.4
Heptanoic	120.9	Elaidic	54.4
Caprylic	125.8	Erucic	51.2
Nonanoic	123.5	Brassidic	51.8
Capric	119.3	Δ²,³-Oleic	1.3

[a] A. Skrabal, "Chemical Kinetics," in International Critical Tables, vol. VII, McGraw-Hill, New York, 1930, p. 138.

for forcing esterifications to completion; broad patents in this field have expired (31).

Alcoholysis. The preparation of esters by reaction of alcohol with ester instead of with acid, resulting in the formation of alcohol and ester instead of water and ester, can be carried out by methods analogous to those used for esterification, with or without catalyst, and with the aid of analogous devices for promoting completeness of reaction. Acid catalysts are effective, as they are for esterification. A notable difference between the two reactions is that the absence of acid as a reactant in alcoholysis makes it possible to use alkaline substances as catalysts. Alkaline catalysts are so remarkably effective that temperatures quite different from those required when no catalyst, or an acid catalyst, is used are appropriate with alkaline catalyst. In many cases room temperature is high enough to give a satisfactory rate; in cases where temperatures above 100°C. are desirable for some reason, the quantity of alkaline catalyst required to give a rapid reaction rate may be minute.

The very rapid rate of alcoholysis tends to obscure the fact that different alcohols and esters may react at considerably different rates in alkaline systems. The same is true of ester-ester interchange. In this connection it is interesting to note the astonishing differences that have been observed in the rates of alkaline saponification of various esters. At one extreme the saponification rate of ethyl oxalate is so rapid that the acid value of a sample of the ester cannot be determined in the ordinary way by titrating it in alcoholic solution with aqueous sodium hydroxide, using phenolphthalein as indicator; the ester starts to saponify before the alkalinity is strong enough to turn the phenolphthalein pink. The saponification rate of ethyl oxalate is more than five million times as great as that of ethyl acetate. At the other extreme the sterically hindered ester, tertiarybutyl 2,4,6-trimethylbenzoate, was not affected at all when boiled for an hour with 20% sodium hydroxide solution (32). Table V shows relative rates for esters of a few different alcohols and acids.

TABLE V

Comparative Rates of Alkaline Hydrolysis of a Few Esters (33)
(Rates relative to that of Ethyl Acetate taken as 100)

Ester	Rate	Ester	Rate
Methyl acetate	155	Ethyl formate	21,300
Ethyl acetate	100	Ethyl propionate	90
n-Butyl acetate	77	Ethyl butyrate	53
iso-Butyl acetate	69	Ethyl caproate [a]	52
sec.-Butyl acetate	16	Ethyl methoxyacetate	1,945
tert.-Butyl acetate	1.6	Ethyl acetoacetate	436
Glycol monoacetate	266	Ethyl pyruvate	1.7×10^6
Monoacetin	316	Ethyl oxalate 1st stage	5.8×10^6
Vinyl acetate	9600	Ethyl oxalate 2nd stage	1,130
Allyl acetate	179	Ethyl benzoate	26
Phenyl acetate	1250	Benzyl acetate	195

[a] In alcohol-water.

The effect of varying the alcohol group is shown by the variation in rate for different acetates. Esters of secondary and tertiary alcohols reacted noticeably more slowly than those of corresponding primary alcohols. Glycol and glycerol acetates saponified significantly more rapidly than ethyl acetate. On the basis of other experience, it may be said that this kind of difference carries over into alcoholysis and ester-ester interchange and that the natural fatty glycerides are relatively responsive to the effect of alkaline catalyst in these reactions. Variations in the

acyl end of the ester may cause extreme differences in rate of saponification, but differences among the esters of normal fatty acids from butyrate upward are negligible. Ethyl butyrate and ethyl laurate saponify at the same rate in 85% alcohol (34).

The variations in esterification rates of different acids and alcohols can be accounted for largely by differences in steric hindrance, but the differences observed in these alkali-catalyzed reactions can hardly be accounted for in this way alone, and evidently other effects are involved. Many of the differences can be attributed to polarity or polarizability of the molecules; it is believed that substituent groups differing in their tendencies to attract or to release electrons differ in their influence on the electron density around the site of reaction and thus affect the rate at which the molecule will react with a highly polar entity, such as hydroxyl ion or alkoxy ion. Resonance also may have an effect, especially when the ester is one in which the carbonyl of the ester group is conjugated with unsaturation in the acyl group. Attempts have been made recently to assign quantitative values to the various effects attributable to molecular structure and to reconcile apparently conflicting views (35, 36).

Ester-ester Interchange. The fact that radicals will exchange in a mixture of esters when they are held at temperatures about 300°C. was known as far back as the time of Friedel and Crafts (40). Since that time much work has been done on this reaction, including tests of many catalysts and numerous attempts to find useful applications of the reaction to fats and fatty materials. Also it has been shown that interchange of radicals occurs as a part of what is happening in other processes, such as varnish cooking and heat-bodying of oils. The reaction may be applied in countless ways to natural or artificial mixtures of triglycerides, to mixtures of fats with fatty or non-fatty esters of alcohols other than glycerol, and indeed to almost any sort of ester mixture in which fatty esters are involved. The history of this work has been reviewed several times (9, 12, 23, 37, 38).

The most important commercial application of the reaction to fats has been to improve lard for use in plastic shortenings. Currently two main types of the reaction are being practiced commercially, both applied to the natural triglyceride mixtures existing in whole lard, and both utilizing highly active alkaline catalysts at moderately low temperatures. The one type, which consists simply of interesterifying the melted lard until an approximate equilibrium has been attained, has been referred to as "randomizing" because it is believed that it produces a triglyceride composition closely approximating that which would be produced if the various fatty acid radicals were distributed purely at random, in accordance with the laws of chance, among the hydroxyl groups of the glycerol. The effect is essentially the same as that which would be obtained if the lard were completely hydrolyzed and re-esterified. The other type of process is carried out at a lower temperature, low enough to allow crystallization of a portion of the mixture while the interchange of radicals is continuing in the liquid portion. This produces a different composition, comprising a larger proportion of high-melting glycerides and a correspondingly larger proportion of very low-melting glycerides. The degree of differ-

ence depends upon the temperature, time, and other conditions of the reaction.

The reason for randomizing lard is that the triglyceride mixture produced by the process has a composition and physical properties different from those of the original lard and that, for the production of certain commercial products, these physical properties are more desirable than those of the original lard. When used to formulate a plastic shortening, usually simply by the addition of a small proportion of "flakes" (low I.V. hydrogenated cottonseed oil, lard, tallow, or other fat), followed by the usual finishing operations, the plasticized product made from randomized lard has a better appearance because it has more and finer crystals, keeps its appearance better during storage, and has better creaming and cake-making qualities, and other properties superior to those of the corresponding shortening made with natural lard (8, 10, 39). Practical methods for applying this process to lard may be typified by the method used by Armour and Company, according to a published description (39). Melted unrefined lard is mixed with filter aid in an agitated tank, pumped at a rate of 30,000 lbs. per hour through a plate filter into a 60,000-lb. holding tank, where it is held at 175–180°F. From this tank the lard goes through a continuous vacuum dryer from which it is pumped to one of a pair of 5,000-lb. closed reactor tanks equipped with steam coils and agitator. Sodium methoxide is added as catalyst, and the reaction is allowed to take place for a "few minutes." The grade and quantity of sodium methoxide is undisclosed, but presumably the catalyst consisted of finely powdered dry sodium methoxide in a quantity not more than about 0.2%. The product from the reactor passes through a strainer and air separator to a small high-velocity mixer, where a fixed proportion of water is added. The mixture passes through a tubular heater at 165°F. to a centrifuge, which removes the heavier foots. The partially clarified lard is run through a skimming tank and through a recirculating hot water wash system, from which it goes through secondary centrifuges and finally through a vacuum drier at 1 to 1.5-in. mercury pressure, after which it is ready for processing into shortening.

This catalyst has the advantages that a short reaction time and a relatively low temperature can be used with only a small expense for catalyst and with little or no darkening of the color of the fat. Similar results can be obtained with other sodium alkoxides and with finely dispersed metallic sodium, sodium potassium alloy (43), and sodium hydride. In every case it is necessary to use a catalyst in such a form that it may be dispersed rapidly and completely in the fat. The actual catalytic material presumably consists of anions of some sort formed in the fat by the added alkaline material, whether it be sodium methoxide, metallic sodium, or some other comparably active alkaline material. In the case of sodium methoxide it can be shown that a quantity of methyl esters, approximately equivalent to the quantity of added catalyst, is formed almost as soon as the catalyst has been thoroughly dispersed in the fat. Many other less active catalysts have been proposed for which a considerably higher reaction temperature is appropriate, but many of them cause the fat to darken or have other disadvantages. A method which

would seem to have practical possibilities but does not appear to have had much use is to heat a fat with a small quantity of glycerol or mono-glyceride and a small quantity of alkaline material, such as sodium hydroxide, sodium carbonate, or sodium soap, at temperatures in the neighborhood of 225°C. (41, 42). A patent recently issued (44) discloses a new method whereby a 50% aqueous solution of sodium hydroxide can be used to form a catalyst in lard sufficiently active to randomize the lard in less than 5 min. at temperatures around 330°F. (165°C.). The alkali solution is dispersed in the fat and instantly dried in a two-stage vacuum drier with reheating between the two stages of the drier. Under these conditions evidently it is possible to form a catalytic anion in the fat before the sodium hydroxide has been able to saponify the fat and be converted completely to soap.

The application of directed interesterification to lard on a commercial scale has been described recently (14). Unrefined lard is preheated and vacuum-dried, then cooled to a temperature just above its melting point by passage through a heat exchanger, whence it goes to a small continuous mixer where a metered stream of liquid catalyst, sodium-potassium alloy, is dispersed in it in small droplets, 10 to 40 microns in diameter. The lard-catalyst mixture is chilled in a scraped-wall heat-exchanger to a temperature low enough to induce crystallization of a portion of the higher-melting glycerides of the mixture. After a short period in a crystallizer, during which the heat of crystallization raises the temperature of the mixture, it is pumped through a second chiller and then passes through a series of four gently agitated crystallizing tanks. The continuous agitation keeps the lard in a flowing state even though a considerable proportion of solid is formed. The product comes from the crystallizers at a temperature between 90 and 100°F., the exact temperature depending upon the desired proportion of fully saturated triglyceride, and is mixed with carbon dioxide and water in a continuous high-speed mixer to destroy the catalyst. The mixture is then melted and freed from soaps by conventional water-washing, centrifuging, and vacuum-drying steps. The product may be partially hydrogenated to improve stability. Shortenings made in this way have the advantages of those made with randomized lard, and in addition they have a better plastic range, that is, a wider range of temperatures within which the shortening will remain neither too soft nor too hard for satisfactory use. In effect, the "flakes" ordinarily added to lard to give a proper consistency are generated from the lard itself, with a corresponding reduction in the quantity of intermediate-melting glycerides.

Both of the types of processing described have many other possible applications, and now that they have been put into successful commercial use in one application, it may be expected that others will follow. The effect of interesterification of glyceride mixtures in a single phase differs in different cases, depending upon the composition of the fat or mixture to which it is applied. The melting point, for example, may be raised or lowered, depending upon the starting composition. If the fat at the start is a high-melting mixture of completely hydrogenated fat with a larger proportion of oil, the effect of interesterification will be to decrease the proportion of trisaturated glycerides and to lower the melting point. Ap-

plied to an oil like cottonseed oil which contains a substantial proportion of solid fatty acids but hardly any trisaturated glyceride, the process will raise the melting point because it increases the proportion of fully saturated glycerides. The compositions that can be produced by this type of process from a given starting-material lie within the range between the starting material and its "randomized" composition. Within this range it is quite possible that practical advantages will be found for products not now being made.

The directed interesterification process increases the number of possibilities for, depending upon how it is applied, it may be used to increase the proportion of high-melting glycerides and to improve plastic range, as in the case just described, or it may be operated in such a way as to increase the proportion of intermediate-melting glycerides and thus change some of the physical properties in an opposite direction. Together the various interesterification processes may be expected to continue to increase the interchangeability of use of the various fats and oils and to make possible the production of improved products.

REFERENCES

1. Leyes, C. E., "Esterification," in Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 5, pp. 776–817, New York, Interscience, 1950.
2. Reid, E. E., "Esterification," in Groggins, P. H., "Unit Processes in Organic Synthesis," ch. X, p. 613, 3rd ed., New York, McGraw-Hill Book Co. Inc., 1947.
3. Goldsmith, H. A., Chem. Revs., 33, 257–349 (1943).
4. Burrell, H., Oil and Soap, 21, 206–211 (1944).
5. Brandner, et al., Ind. and Eng. Chem., 37, 809–812 (1945).
6. Corn Products Refining Company, Technical Bulletin R3-5 (1954).
7. Bradshaw, G. B., and Meuly, W. C., U. S. Patent 2,360,844 (1944).
8. Bailey, A. E., "Industrial Oil and Fat Products," pp. 282–284, 208, 213–215, 229–230, 682, 1st ed., New York, Interscience Publishers Inc., 1945.
9. ibid., pp. 681–686.
10. Vander Wal, R. J., and Van Akkeren, L. A., U. S. Patent Re 23,499 (1952).
11. Mattil, K. F., and Norris, F. A., U. S. Patent 2,625,478 (1953).
12. Eckey, E. W., Ind. and Eng. Chem., 40, 1183–1190 (1948).
13. Eckey, E. W., and Formo, M. W., J. Am. Oil Chemists' Soc., 26, 207–211 (1949).
14. Hawley, H. K., and Holman, G. W., J. Am. Oil Chemists' Soc., 33, 29–35 (1956).
15. Hoerr, C. W., and Waugh, D. F., J. Am. Oil Chemists' Soc., 32, 37–41 (1955).
16. Carter, R. P., Ind. and Eng. Chem., 37, 448–50 (1945).
17. Hind, J. D., et al., Ind. and Eng. Chem., 46, 441–52 (1954).
18. Feuge, R. O., and Bailey, A. E., Oil and Soap, 23, 259–64 (1946).
19. Runk, R. H., Ind. and Eng. Chem., 44, 1124–26 (1952).
20. Kienle, R. H., et al., Ind. and Eng. Chem., 41, 716–740 (1949).
21. Dunlap, L. H., et al., J. Am. Oil Chemists' Soc., 27, 361–366 (1950).
22. Mueller, E. R., et al., Ind. and Eng. Chem., 42, 1532–36 (1950).
23. Formo, M. W., J. Am. Oil Chemists' Soc., 31, 548–59 (1954).
24. Archer-Daniels-Midland Company, Bulletin No. 907R, pp. 4–5 (1956).
25. Konen, J. C., et al., Oil and Soap, 22, 57–60 (1945).
26. Chablay, A., Compt. rend., 239, 172–73 (1954).
27. Feuge, R. O., et al., J. Am. Oil Chemists' Soc., 22, 202–207 (1945).
28. Loening, K. L., Garrett, A. B., and Newman, M. S., J. Am. Chem. Soc., 74, 3931 (1952).
29. Smith, H. A., and Burn, J., J. Am. Chem. Soc., 66, 1496 (1944).
30. Aelony, D., J. Am. Oil Chemists' Soc., 32, 170–172 (1955).
31. Graves, G. D., U. S. Patents 1,882,808 (1932); 1,860,092 (1932).
32. Cohen, S. G., and Schneider, A., J. Am. Chem. Soc., 63, 3382–88 (1941).
33. Olsson, H., Z. physik. Chem., 133, 233 (1928).
34. Levenson, H. S., and Smith, H. A., J. Am. Chem. Soc., 62, 1556–58 (1940).
35. Taft, R. W. Jr., J. Am. Chem. Soc., 74, 2729–32, 3120–28 (1952).
36. Taft, R. W. Jr., J. Am. Chem. Soc., 75, 4231–38, 4534–37, 4538–39 (1953).
37. Eckey, E. W., "Vegetable Fats and Oils," pp. 142–149, New York, Reinhold Publishing Corp., 1954.
38. Bailey, A. E., "Industrial Oil and Fat Products," ch. XIX, 2nd ed., New York, Interscience Publishers Inc., 1951.
39. Slater, L. E., Food Engineering, 25, No. 9, 72–73, 100–105 (1953).
40. Friedel and Crafts, Ann., 133, 207–11 (1865).
41. Gooding, C. M., U. S. Patent 2,309,949 (1943).
42. Bailey, A. E., et al., Oil and Soap, 20, 132 (1943).
43. Hawley, H. K., and Dobson, R. D., U. S. Patent 2,733,251 (1956).
44. Holman, G. W., et al., U. S. Patent 2,738,278 (1956).

Outline of Processes Used in the Drying of Soaps and Detergents

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BECAUSE OF THE MAGNITUDE of the subject this discussion will be confined to those processes in which there is a significant reduction in the moisture content of the product. This will eliminate from consideration the subjects of "skin drying" of bar soaps and the so-called chemical drying in which moisture is merely "fixed" as water of crystallization.

A classification of all drying systems used by industry would include about 20 separate and fairly distinct methods and apparatus for the reduction of moisture in a wide variety of products. Only four of these systems have attained significant application in soap and detergent processing. With the approximate dates of their commercial application to soaps and detergents, they are conveyor drying, about 1894; spray drying, about 1920; drum drying, about 1930; flash drying, about 1937.

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In the soap and detergent industry the drying processes perform an important function other than the simple reduction of moisture, i.e., in many cases they are the final or finishing process and as such are responsible for the physical form in which the products appear on the market. They have also a considerable influence on such other important characteristics as solubility and density. Over the long term the industry has been working toward the development of forms that make for improved solubility, and these processes have made significant contributions toward that end.

According to the latest available statistics, the total production of soaps and detergents in this country for the year 1955 approximated four billion lbs., of which, two-and-three-quarter billion lbs. were finished in the drying process. The above figures indicate an industry drying capacity approaching ten million lbs. a day.

The story of the drying processes in our industry is largely that of invention and development of specialized types of equipment as well as adaptation and modification of existing machinery. In the drying field some of the most important developments have come from within the industry. In a description of the four processes used for drying there will be a brief description of the most modern equipment,