Textile Assistants from Fatty Acids and Their Derivatives

E. D. McLEOD, Arnold, Hoffman and Company, Cincinnati, Ohio

FATTY oils and acids have long been known to the textile industry, being used in the various steps of processing fibers from scouring through to the finished fabric. Earlier use was chiefly confined to oils, fatty acids, and their soaps, and as such were useful assistants in scouring, lubricating, and dyeing operations. Development of derivatives of the fatty acids has opened up new fields and greatly increased their value to the textile industry. Whereas one used to hear only of anionic compounds, we now hear products referred to as anionic, cationic, and non-ionic. All three groups have their place in the processing of cotton, wool, and synthetic fibers.

Fatty acids are obtained by hydrolysis of their glycerides to yield glycerine and the corresponding fatty acids. All fatty acids fall into one of two groups: saturated, represented by stearic, and unsaturated, represented by oleic. Unsaturated acids are normally used in processing prior to finishing while saturated acids and derivatives are more acceptable for finishing operations. Oils and acids with iodine value exceeding 100 are not generally used, on account of oxidation reaction at the unsaturated linkage which results in odor development and discoloration of white goods.

There are available for textile processing many fatty acids and their derivatives, a few of the acids being:

Coconut	Stearic	Azelaic
Lauric	Oleic	Pelargonic
Myristic	Palmitic	Tall Oil Acids

Economics are a controlling factor in their uses, and generally the industry favors stearic, oleic, tall oil acids, coconut, or their derivatives. Lauric, palmitic, and myristic acids find specific uses. Recent developments by Emery Industries have made available azelaic and pelargonic acids through ozonization of oleic acid. These two new acids are rapidly finding use in the plasticizer field. Tall oil acid, a mixture of oleic and resin acids, offers a cheap source of raw materials, but its use is confined to prefinishing operations due to its inherent characteristics. Stearic, oleic, and coconut fatty acids are widely used, and this paper will discuss their uses in processing textiles.

The first use of stearic and oleic acids was as softeners and soaps, respectively. Stearic acid softeners are still used today, but the development of amides and other derivatives for semi-permanent or permanent finishes has replaced the early softeners. Sodium and potassium oleates are used for scouring, sharing the field with the synthetic detergents. Economics again play an important part, and red oil soaps are used as long as the price of fats remains competitive. One mill reported a few years ago that red oil soaps were used as long as red oil did not exceed 18-19c per pound, but when this cost was reached, synthetic detergents were used.

The use of fatty compounds in the textile industry may be classified according to their functions, namely, lubrication, plasticizing, defoaming, scouring, softening, wetting and rewetting, and emulsifying.

In these functions fatty acids find uses as such or through a derivative. The major derivatives of interest in the textile industry are as follows: soaps of the alkali metals and amines, esters and their sulfates, sulfated fatty alcohols, sulfated oils, ethylene oxide condensates, fatty amides, and quaternaries.

All of the above compounds contribute to the proper processing of textiles from the fiber to the finished cloth. In the manufacture of textiles, operations using fatty acids or their derivatives are: scouring, spinning, sizing, dyeing, and finishing.

Scouring processes are well established for wool, cotton, or synthetic fibers. Raw wool may be scoured through use of sodium oleate and small amounts of alkali, such as soda ash or ammonia, or non-ionic products, such as ethylene oxide condensates. Sodium oleate is easily prepared by saponification of the oleic acid with sodium hydroxide; a low titre red oil is preferred in order to reduce the stearic acid content as much as possible. Kier boiling of cotton is assisted by the use of sodium oleate soap and caustic. Ethylene oxide condensates of fatty alcohols are finding more use as scouring agents, being milder in this effect on the fiber and resulting in less damage. These condensates are particularly effective on cotton and synthetic fibers, with very low percentages of the active compound being necessary. One of the outstanding features of the ethylene oxide condensates of fatty acids, amides, or alcohols is their resistance to alkaline earth metals present in hard water, such as calcium and magnesium.

Other groups of compounds particularly effective in scouring are the sulfated alcohols and sulfated alkylol amides. These two groups also possess resistance to hard water and find widespread use in the industry. One of the earlier sulfated fatty amides was the sulfated monoethanolamide of coconut fatty acid sold under the trade name of Intramine. It is easily manufactured by first forming the amide, followed by sulfation and conversion to the sodium salt. Its formation may be represented as follows:

$$C_{11}H_{22}COOH + NH_2CH_2CH_2OH \longrightarrow C_{11}H_{22}\overset{O}{\overset{\|}{C}}-NH-CH_2CH_2OH + H_2O$$

$$C_{11}H_{22}\overset{O}{\overset{\|}{C}}-NHCH_2CH_2OH \xrightarrow{H_2SO_4} C_{11}H_{22}\overset{O}{\overset{\|}{C}}-NH-CH_2CH_2OSO_3H + H_2O$$

$$\downarrow NaOH$$

$$C_{11}H_{22}\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2OSO_3Na$$

Lubrication of fibers is of vital importance for wool, cotton, and synthetics. In the case of wool and synthetics, the lubricant used must be easily removed by mild scouring whereas cotton can withstand stronger treatment. Mixtures containing yellow mineral oil, "mahogany soaps," red oil, and coupling agents are widely used on woolens, yarns, and reworked wool. A typical formula for an oil to be used on reworked wool would be 80-85% of 100 vis. mineral oil and 15-20% of potassium oleate, oleic acid, H_2O, and coupling agent. In the case of a petroleum sulphonate base, the percentage of red oil as soap or fatty acid would be lower. Cotton lubricants usually contain high percentages of mineral oil with oleate soap and/or petroleum soaps as an emulsifier.

The use of ethylene oxide condensates of amides, alcohols, or fatty acids as emulsifiers for lubricant mixtures or directly as a lubricant in some cases has been of considerable interest to the industry. In rayon spinning, one of the oldest nozzle lubricants has been lauryl pyridinium chloride. Lubrication of rayon and other synthetic fibers consumes a great deal of refined or white mineral oil containing a balanced emulsifier designed to produce a stable emulsion of given viscosity suitable for application to the filament and easily removed in subsequent scouring operations. Earlier formulas contained white mineral oil, oleate soaps, coupling agents, and sulfated oils. As techniques have been improved and machinery speeded up, static electricity has been a big problem to dispel. Several formulations are available today containing ethylene oxide condensates of fatty acids or their derivatives, which are effective anti-static agents. Of these, the condensates of fatty alcohols, such as oleyl or cetyl, have attracted a great deal of interest.

In sizing, fats and oils are used as plasticizers and emulsifiers. Sulfated tallow is one of the more commonly used ingredients for plasticizing starch. In sizing rayon, gelatine is used a great deal as the basic material, which is plasticized with oils containing mineral oils and fats. Here again, ethylene oxide condensates are of interest, but they must be carefully selected as certain types are not compatible with gelatine. Oxidation of the lubricant must be prevented either by starting with a saturated fat base or proper selection of an antioxidant which will prevent development of color and rancid odor in the lubricant and size mixture. Many antioxidants are available and are very effective; the majority are based on phenol or its derivatives.

The uses for fatty acids so far have indicated contributions to prefinishing operations in which, for the most part, products used have been removed prior to further treatment. Fatty acids and/or their derivatives have an important part in the dyeing and finishing of fabrics.

Fabrics which are to be dyed may be stock-dyed before spinning in staple form, pigmented in the "dope" stage as in synthetics or piece-dyed after weaving. In addition, millions of yards are printed by means of high speed machines or by hand in the case of block prints for scarfs, handkerchiefs, etc.

Sulfated oils, particularly castor, have been used for a long period of time as assistants in dyeing when moderate surface-active properties aid in producing a level dyeing on the fabric. These oils have suffered from low resistance to hard water but are still finding considerable use. During the past 10-15 years a series of wetting agents based on fats have been developed, which have found wide use in dyeing and printing operations. These products, based on fatty acids or their derivatives, are sulfated fatty alcohols, fatty amides, fatty esters, and ethylene oxide condensates of fatty acids, alcohols, and amides. All of these products have good hard-water resistance, but the sulfated fatty acid esters, as might be expected, are sensitive to alkali. Relatively small amounts of these materials are necessary, the usual quantities being (.1-.25%) on the weight of goods being dyed.

Certain surface-active agents possess the property of rewetting rapidly after the cloth is dried while others are relatively slow. A class of compounds which rewet rapidly are sulfated fatty acids and fatty acid esters, of which the esters offer better efficiency and stability to hard water. Products of the fatty acid ester type are sold under such trade names as Ahcowet RS, Surfax WO, and Warcosan. For the most part they may be represented by the following formula:

$$\begin{array}{l} \quad\;\; O \\ \quad\;\; \| \\ R-C-O-R' \\ | \\ OSO_3Na \end{array}$$

in which R is an unsaturated fatty acid sulfated at the double bond and R′ is a short alkyl chain such as methyl, butyl, or amyl. The presence of saturated acids will result in lower surface-active properties and should be avoided if possible. For example, in the case of an oleate ester of low titre oil is desirable. Manufacturing processes can be altered to produce wetting agents of exceptional resistance to hard water, fast wetting-out properties, but poor rewetting ability. In Sanforizing, fast rewetting is essential, and cloth padded with the rewetting agent and dried must be capable of rewetting instantly as it passes through water sprays prior to the pre-shrinking operation. Red oil (oleic acid) and its derivatives are used extensively here.

After the dyeing or printing stage, fabrics are finished to the desired "hand," such as soft in the case of dress goods, stiff for chintz, and water-repellent for winter sports or rain garments. All of these finishing operations consume large quantities of fats or their acid derivatives.

Sulfated tallow, olive oil, and other glycerides have long been used as softening agents for finishing fabrics. Sulfated tallow is used today on fabric lines which are not considered to have a permanent finish. Through use of sulfated oils a pleasant soft finish is obtained, but it is removed by the first cleaning operation. Since 1935 a series of fatty derivatives have been developed which are substantives to cotton and synthetic fibers. The products may be cationic or anionic, depending on their synthesis. For softening, stearic acid derivatives are excellent, yielding high softening per unit weight.

The development of new softeners of the substantive type has been based on the theory that compounds containing primary, secondary, or tertiary nitrogens are substantive to cotton, rayon, and other synthetic fibers. There are available today many fatty acids for combining with organic amines, such as ethylenediamine, monoethanolamine, etc., but for finishing purposes the use of unsaturated acids is not advisable. For example, an amide of oleic acid will soften a piece of cloth but will tend to discolor white goods and, upon subjection of the fabric to aging tests, will discolor, due to oxidation of the unsaturated chain present. Development containing only small amounts of linoleic and linolenic acid gives increased resistance to oxidation but still will not yield the softening power per unit weight obtained when stearic acid is used in the compound. Of the saturated acids available for use in these amides, stearic is the best although coconut, lauric, and myristic acids offer good softening and low discoloration under aging conditions. On the basis of available literature and acceptance in the textile industry, stearic acid offers the best starting fatty acid for synthesis of a substantive softener.

Organic alkyl or alkylol amines are readily available, ranging from tetraethylene pentamine to monoethanolamine, with several companies offering various alkylol amines and polyamines. The corresponding amides of stearic acid are easily formed by heating the mixture of fatty acid and amine to a temperature of 125-165°C., during which time the amine soap is formed, followed by formation of the amide with loss of one molecule of water. The formation of an amide may be represented as below:

$$\underset{\text{Stearic Acid}}{C_{17}H_{35}COOH} + \underset{\text{Ethylenediamine}}{NH_2-CH_2-CH_2-NH_2} \xrightarrow{\Delta}$$

$$\underset{\text{Amino Ethyl Stearamide}}{C_{17}H_{35}-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_2-NH_2} + \underset{\text{Water}}{H_2O}$$

This product is a hard, waxy substance with a melting point of approximately 126°C. By varying the organic amine used, the melting point of the amide can be varied from about 55°C. to 126°C. The amides thus formed possess little, if any, solubility in water and must be alkylated, treated with acid, such as acetic, or converted to an alkali salt (5). As would be expected, the higher the melting point of the amide, the more difficult it is to produce a workable water paste for use in the mill. Products with melting points in excess of 90-95°C. are very difficult to disperse, and for the most part amides with melting points in the range of 55-75°C. are preferred. It is possible to increase the molecular ratio of stearic to organic amine from 1:1 to 2:1, but the products thus obtained are very difficult to disperse due to their high molecular weight.

It has been shown that fatty amides containing primary and/or secondary nitrogen tend to be less resistant to aging. A series of products in which the primary and secondary nitrogens were reacted with urea were developed by Morgan and McLeod (5). A carbamate compound is formed.

From the above developments substantive softeners, both cationic and anionic, may be obtained. The cationic softeners have the disadvantage of adversely affecting the light fastness of certain dyes, as compared to no effect when using an anionic type (5). By treatment of the fatty amide with strong alkali, the alkali metal salt is formed through the weakly acidic hydrogen attached to the nitrogen at the amide or carbamate linkage. The alkali metal salts do not affect the light fastness of dyestuffs. In addition to this group of products, certain non-substantive types are of interest.

Long chain alcohol sulfates and ethylene oxide condensates of alcohols, fatty acids, esters, and amides are used, but none of these products is durable, being removed the first time the fabric is laundered.

In application the non-durable type softeners are applied by padding in 1-2% solutions. The substantive types may be padded but generally are applied in the dye bath in the last rinse by exhaustion onto the fiber.

Scrooping agents represent another field in which fat-based products are used. Here ethylene oxide condensates of stearic acid have shown promise either by themselves or as emulsifiers for water-insoluble alcohols.

Water-repellent finishes for textiles consume fats, either as emulsifiers for the non-durable wax emulsion types or as the main portion of the finish in the case of the durable products. Drax, offered by S. C. Johnson and Son Inc., is a wax emulsion type on the market while products such as Velan, Zelan, and Norane are the durable types. The durable types are impregnated on the cloth from a water solution, dried at relatively low temperatures, and cured at elevated temperatures, leaving a water-insoluble coating on the fabric.

In reviewing the textile field, one can see that fat-based products play a very important part in the clothes we wear every day. The last 10 to 15 years have seen the industry come a long way, and without the help of new fatty derivatives this would not have been possible. Higher and higher speeds demanded by the industry to help in the fight against increased costs have raised new problems in lubrication, static control, etc. The development of fat-based derivatives in the fields of lubricants, detergents, emulsifiers, wetting agents, and finishing compounds presents a challenge to a research man.

Acknowledgments

These are made to W. C. Hardesty Co. Inc., Armour and Company, and Emery Industries Inc.

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