Interfacial Phenomena In Use Of Detergents And Cosmetics

P. Somasundaran
Henry Krumb School of Mines,
Columbia University, New York, N.Y. 100027.
and
Department of Metallurgy. Indian Institute of
Science, Bangalore-560 012.

Introduction

Detergency is essentially an interfacial phenomenon and so is the successful application of cosmetics. In these cases the systems must possess given interfacial properties that might be different for different types of products. Some should have good wetting properties, whereas some others should possess emulsifying or foaming properties, all to different extents, again depending on the products desired. The desired interfacial properties are achieved by use of chemicals known as surfactants. These chemicals are characterized by their tendency to concentrate at an interface and thereby alter the free energy of the interface and often other important properties such as interfacial viscosity and electrical charge.

Surfactants

Use of appropriate surfactants in desired concentrations permits their use as detergents for removal of soiled and oily matter from fabric or human skin and hair, wetting agents for hair colourants and emulsifying agents for creams etc. Common soap is the most familiar example of a surfactant which is composed of at least one part that prefers to be in an oil phase and one that prefers to be in water. The former, known as hydrophobic (water-hating), acquires its property due to the presence of methyl ($-CH_3$) or methylene ($-CH_3$-) or benzyl ($-C_6H_5$) groups etc., in the form of hydrocarbon chain, and the latter, known as hydrophilic (water-loving), due to the presence of polar groups such as $-OH$, $-SO^-_3$, $-COO^-$, or $-NH_3$+. Thus oleate that is present in common soap has the structure

$$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COO.$$

where COO- is the hydrophilic part due to the ionic nature of it, and the rest of it is the hydrophobic part, which owes its preference to oil phase due to the presence of the $-CH_2$-, $-CH_3$ and $-CH=$ groups. The use of the term "hydrophobic" might not strictly be correct, since even between the $-CH_2$- groups in the hydrocarbon chain and the $-OH$ groups in water there will be a certain amount of van der Waals attractive forces in existence. It is the greater attractive interactions between the $-CH_2$- groups of the surfactant and $-CH_2$- or other non-polar groups of an oil phase that, however, make the "hydrophobic" part prefer the oil phase. There are essentially four types of surfactants, anionics that possess a net negative charge, cationics that possess a new positive charge, non-ionics that possess no new charge, and ampholytes that can possess either a negative or positive charge depending upon the solution conditions. Examples(1) of anionic surfactants with different structural make-up used in cosmetics are fatty acid soaps (RCOO- M+), alkyl sulfates (RSO^-_4 M+), benzyl sulfonates ($RC_6H_4SO_3$- M+), monoglyceride sulfates ($RCOOCH_2CHOH\ CH_2SO^-_4$ M+) and alkylether sulfates. R is the hydrocarbon chain tat normally contains 10 to 18 carbon atoms and M+ represents a cation such as K+, Na+ or Al+++ or triethanol amine. Anionics have excellent cleansing and foaming properties and, therefore, are used widely as laundry detergents, shampoos, shaving creams and dentifrices. Typical examples of cationic surfactants are alkyltrimethyl ammonium salts ($R\ N^+(CH_3)_3\ X^-$), quarternary amide of ethylenediamine ($R\ CONH\ CH_2\ CH_2\ N^+\ (CH_3)_3\ X^-$) and alkylpyridinium salts ($R\ N\text{-}C_6H_4\ X^-$); X- represents an anion such as Br-, Cl- or acetate. These surfactants, due to their positive charge, can adsorb on negatively charged surfaces such as hair and modify their behaviour. They therefore find application as hair conditioners. They are also reported to have germicidal properties and find use also in anti-dandruff preparations. Non-ionic surfactants of interest include fatty acid alkanolamides ($R\ CONH\ CH_2CH_2OH$) alkylpolyglycol ethers ($R\ (OCH_2CH_2)nOH$, polyethylene oxide alkyl phenols ($R\ C_6H_4\ (OCH_2CH_2O)n\ CH_2CH_2OH$) and alkyl polyethyleneimine ($R\ (NHCH_2CH_2)nNH_2$). Non-ionic surfactants can modify such properties as interfacial viscosity significantly in the presence of ionic surfactants, and are used, for example, as emulsion stabilizers in the manufacture of creams etc. Their solubility properties also enable them to be used as solubilizers for colorants, perfumes etc. Finally, the ampholytic surfactants can be illustrated with the typical example of an alkylamine acid s alkylaminoproprionate ($R\text{-}NH_2CH_2CH_2COO_-$). Ampholytes, due to their reported mild action, find use in baby shampoos.

Basic Principles

A knowledge of interfacial phenomena and the mechanisms by which interfacial properties can be altered is essential for proper development of cosmetics and detergents. Even though aften considered as a plane, interface is actually a region at the boundary of phases where the system properties will be different from that of the bulk. Type of possible interfaces are solid/liquid, liquid/liquid, solid/solid, solid/gas and liquid/gas. In addition, in detergency properties of the line contact between three phases (solid/liquid/liquid or solid/solid/liquid) can also become important. Chemical species at the interface possess a higher free energy than those in the bulk and this excess free energy (essentially due to the existence of an interface) is known as interfacial energy or surface energy. There is indeed an increase in the total energy of the system due to the existence of this interfacial energy, the increase being proportional to the total area of the interface. A system always tries to reduce its total free energy. The tension that exists at the interface to reduce the total surface area, and thereby the increase in energy, is known as interfacial tension or surface tension. Minimization of this interfacial tension is important in the formulation of stable cosmetics, since most cosmetics are emulsions made up of minute droplets of oil in water or water in oil and hence possess a large interfacial area. Such minimization can be achieved by the addition of surfactants that will have a tendency to concentrate at the interface due to the affinity of one part of it to the oil phase and the other part to the water phase. The surface tension decreases with the addition of a surfactant till a limited value (critical micelle concentration) is reached at a specific conentration. Addition of surfactants in larger amounts results in the formation of surfactant aggregates known as micelles. Micelles will have the hydrophilic part of the surfactant oriented towards the aqueous phase, and the hydrophobic part away from it. Thus a micelle in water has a hydrocarbon interior that can solubilize significant quantities of other hydrocarbon species, a phenomenon that is considered important in detergency. These other interfacial phenomena that are relevant here are adsorption, interfacial viscosity and zeta potential. Like at liquid/air and liquid/liquid interfaces, surfactants can adsorb also on solid due to favourable energy of interaction between them and the solid. Such adsorption can significantly alter their wetting and hence desoiling properties. The adsorbed surfactant layer can exist either as loose gaseous film, liquified films, or even as a rigid solidified film, depending on the nature of interactions between them. With significant amount of co-operative interaction between the molecules, rigid films with essentially very high interfacial viscosity can result. Such viscosities are often an essential property for cosmetic emulsions. It can help minimize the coalescence between emulsion droplets and thus increase its stability and life.

Adsorption of charged species result in a charged interface, the nature and magnitude of which will largely determine the extent of attractive and repulsive interactions between interfaces. Thus coagulation between emulsion droplets in cosmetics can be retarded by allowing a charged interface to form on the emulsion droplets. The charge at the interface is indeed balanced by ions of opposite charge, known as counter ions, that exist in solution. Addition of salts causes crowding of counter ions in the interfacial region and effectively reduces the extent of interfacial repulsions between charged droplets.

The properties described above comprise a set of fundamental properties that are important in detergency and cosmetics. In addition, a number of other properties such as roughness and porosity of the substrate, hardness of the water, fore find application as hair conditioners. They are also reported to have germicidal properties and find use also in anti-dandruff preparations. Non-ionic surfactants of interest include fatty acid alkanolamides (R CONH CH_2CH_2OH) alkylpolyglycol ethers (R $(OCH_2CH_2)nOH$, polyethylene oxide alkyl phenols (R C_6H_4 $(OCH_2CH_2O)n$ CH_2CH_2OH) and alkyl polyethyleneimine (R $(NHCH_2CH_2)nNH_2$). Non-ionic surfactants can modify such properties as interfacial viscosity significantly in the presence of ionic surfactants, and are used, for example, as emulsion stabilizers in the manufacture of creams etc. Their solubility properties also enable them to be used as solubilizers for colorants, perfumes etc. Finally, the ampholytic surfactants can be illustrated with the typical example of an alkylamine acid s alkylaminoproprionate ($R\text{-}NH_2CH_2CH_2COO^-$). Ampholytes, due to their reported mild action, find use in baby shampoos.

Basic Principles

A knowledge of interfacial phenomena and the mechanisms by which interfacial properties can be altered is essential for proper development of cosmetics and detergents. Even though aften considered as a plane, interface is actually a region at the boundary of phases where the system properties will be different from that of the bulk. Type of possible interfaces are solid/liquid, liquid/liquid, solid/solid, solid/gas and liquid/gas. In addition, in detergency properties of the line contact between three phases (solid/liquid/liquid or solid/solid/liquid) can also become important. Chemical species at the interface possess a higher free energy than those in the bulk and this excess free energy (essentially due to the existence of an interface) is known as interfacial energy or surface energy. There is indeed an increase in the total energy of the system due to the existence of this interfacial energy, the increase being proportional to the total area of the interface. A system always tries to reduce its total free energy. The tension that exists at the interface to reduce the total surface area, and thereby the increase in energy, is known as interfacial tension or surface tension. Minimization of this interfacial tension is important in the formulation of stable cosmetics, since most cosmetics are emulsions made up of minute droplets of oil in water or water in oil and hence possess a large interfacial area. Such minimization can be achieved by the addition of surfactants that will have a tendency to concentrate at the interface due to the affinity of one part of it to the oil phase and the other part to the water phase. The surface tension decreases with the addition of a surfactant till a limited value (critical micelle concentration) is reached at a specific conentration. Addition of surfactants in larger amounts results in the formation of surfactant aggregates known as micelles. Micelles will have the hydrophilic part of the surfactant oriented towards the aqueous phase, and the hydrophobic part away from it. Thus a micelle in water has a hydrocarbon interior that can solubilize significant quantities of other hydrocarbon species, a phenomenon that is considered important in detergency. These other interfacial phenomena that are relevant here are adsorption, interfacial viscosity and zeta potential. Like at liquid/air and liquid/liquid interfaces, surfactants can adsorb also on solid due to favourable energy of interaction between them and the solid. Such adsorption can significantly alter their wetting and hence desoiling properties. The adsorbed surfactant layer can exist either as loose gaseous film, liquified films, or even as a rigid solidified film, depending on the nature of interactions between them. With significant amount of cooperative interaction between the molecules. rigid films with essentially very high interfacial viscosity can result. Such viscosities are often an essential property for cosmetic emulsions. It can help minimize the coalescence between emulsion droplets and thus increase its stability and life.

Adsorption of charged species result in a charged interface, the nature and magnitude of which will largely determine the extent of attractive and repulsive interactions between interfaces. Thus coagulation between emulsion droplets in cosmetics can be retarded by allowing a charged interface to form on the emulsion droplets. The charge at the interface is indeed balanced by ions of opposite charge, known as counter ions, that exist in solution. Addition of salts causes crowding of counter ions in the interfacial region and effectively reduces the extent of interfacial repulsions between charged droplets.

The properties described above comprise a set of fundamental properties that are important in detergency and cosmetics. In addition, a number of other properties such as roughness and porosity of the substrate, hardness of the water,

composition of soiling matter etc., can also have a governing role in the above processes. With the above background, we shall now briefly examine major mechanisms involved in detergency and cosmetics.

Detergency

When a soiled fabric or any other substrate is contacted with detergent solution, first air is displaced from the surface (1, 4, 10, 13, 14). Small air bubbles trapped are removed later during agitation or beating. Next the oily dirt is removed by the spreading detergennt solution. Here the detergent, with its strong tendency to adsorb on the substrate, is able to remove the oily dirt which rolls up to form beads and gets detached from the surface.

Solubilization of oily matter into the detergent micelle is also possible above the critical micelle concentration, which is invariably achieved under most laundering conditions. A similar possibility is penetration of oily dirt by detergent species leading to the formation of a liquid crystaline phase which is often followed by dispersion or dissolution of it into the water. Stevenson(13) has suggested that penetration plays a significant role in most cases.

Osmotic Effects

If the dirt contains any water soluble matter, then condition is also favourable for the osmotic flow of water into the soil. Such seepage of water can cause swelling of the dirt matter and eventual dispersion or detachment of it(13). Detachment of inorganic matter or strongly bound organic matter is often attained only with the help of mechanical agitation. Indeed, wiping with the two surfaces in contact with each other is sometimes necessary to remove strongly held matter.

Redisposition

It is, of course, important that once the dirt is removed it should not redeposit on the surface. The wash liquor will normaly contain oil droplets, dissolved oily an other matter, dispersed particulates and pigment matter. To prevent redeposition, one can control the surface charge of various substrates in such a way that they will repel each other. Most fabrics, for example, will have a negative charge on their surface due to carboxyl groups originally present(18). Dirt dispersed in water will also normally have such a charge due to a detergent layer adsorbed on its surface. Indeed, the presence of non-ionic detergents, use of hot water (which usually leaves less detergent adsorbed on the fabric) etc., enhence the chance of redesposition(13).

Foaming

Foaming, in addition to being a necessary requisite in the eyes of housewives, can assist removal of oil during laundering due to pressure waves generated on the oily surface by a moving foam(13). The pressure waves have their origin due to the pressure differential that normally exists at curved interfaces of films.

Builders

A severe problem in detergency is that caused by the presence of calcium and magnesium. Such divalent species present in hard water can strongly bind dirt to fibre and make it difficult to clean. In order to overcome this problem, reagents (known as builders), such as phosphates, are normally used. Builders act by complexing the calcium, magnesium etc., and thus reduce the effect of their presence. The use of aluminosilicates (zeolites) announced by Proctor and Gamble and Hennel as a partial replacement for phosphate has been possibly the major development in the detergent industry in the last few years(3). The need for a substitute for phosphate arose from the realization of ecological problems caused by the phosphate. Legislations restricting the use of phosphates have also helped the use of heavy duty laundry liquid(9) (HDL). HDLs have enjoyed tremendous acceptance in the U.S. during the last few years due to convenience in using, use as pre-spotters in heavily soiled fabrics, rapid dissolution in cold water etc. HDLs usually contain 10-15% anionic or non-ionic surfactant and 20-30% of a builder such as sodium citrate.

Emulsification

Emulsification used in cosmetics are mostly dispersions of globules of oil in water (o/w) and, to a minor extent, that of water droplets in oil (w/o). The appearance of the emulsion is dependent essentially on the particle size of the droplets. If particles are 1 micron in size or bigger, it will be white, between 1 micron and 0.1 micron, it will be bluish white, between 0.1 and 0.05 microns(it will be semitransparent and with particles smaller than 0.05 microns, a transparent product is the result. When oil and water are mixed, the two phases will separate, but the separation can be delayed even for years with the addition of emulsifying agents. The emulsifier acts by adsorbing at the interface and thus by reducing the interfacial energy. It is the existence of this interfacial energy that is essentially responsible for the instability of an emulsion, since the large increase in interfacial area upon the formation of the emulsion droplets will cause an increase in the free energy of the system. It has also been proposed that adsorption of certain agents can momentarily produce a negative interfacial tension, a condition which is favourable for an increase in interfacial area and hence emulsification. In addition, certain emulsifying agents stabilize emulsions by causing the formation of a rather rigid interfacial film, and also by allowing the generation of electrical charge at the interface. The type of emulsion obtained can be predicted usually with the help of what is known as hydrophile-Lipophile balance (HLB). Surfactants contain both hydrophilic and hydrophobic groups and HLB values tell one about the balance of the forces due to these groups. HLB value for a surfactant can be calculated using the formula:

HLB = sum of hydrophilic group numbers —n + 7. where n is the group number for CH_2 group. Typical group numbers are given below(5) —SO-Na+, 38.7; —COO-K+, 21.1; N(tertiary amine), 9.4; —COOH, 2.1; —OH (Free), 1.9; —OH (Sorbitan ring), 0.5; —CH- or —CH_2- or CH_3-, —0.475, —(CH_2+CH_2—0)-, 0.33, —(CH_2—CH_2—CH_2—0)-, —0.15.

HLB values of selected surfactants on this basis are 40 for sodium lanryl sulfate, 20 for potassium oleate, 11.2 for sucrose monostearate, 8.4 for methanol, 7.2 for sorbitan monooleate, 3.7 for glycerol monostrearate and 1.3 for cetyl alcohol. Molecules that have a low HLB number (4 to 6) are soluble or dispersible in oil and usually give a water in oil emulsion. Those that have a high HLB value (8 to 18) on the other hand are soluble or dispersible in water and give rise to oil in water emulsion. Surfactants with HLB values in the range of 7 to 9 are commonly used as wetting agents and those with values in the range of 13 to 15 function as detergents.

Cosmetics

Cosmetics are different surfactants depending on the intended purpose of the product. Shampoo used for cleaning hair etc. is essentially a detergent solution. Even though common soap will act as a good detergent, in order that it can be effectively used also in hard water areas, synthetic detergents that are insensitive to Ca++, Mg++ etc. are most commonly used in shampoos(6). Since the public wrongly believes that lathering action is a necessary requirement for cleansing, an excessive amount of detergent is usually used. Use of such formulations unfortunately over-clean the hair, removing some of the natural fatty substances; this often makes the hair unmanageable and requires the use of what are known as conditioning agents in shampoos. These contain a number of chemicals, such as lanolin, cetyl alcohol, vegetable oils etc. Conditioners made up of cationic surfactants and, sometimes, protein-based materials are also commonly used after shampooing.

Certain products such as lipstick of course necessarily have special requirements. Firstly, none of the ingredients should be toxic. Secondly, the organic medium should disperse the pigment matter, dissolve fluoresceins, should not have any objectionable odour or taste and should have appropriate vapour pressure lest the problems of sweating, bleeding and drying out occur during the use.

Cosmetic creams are liquid or solid emulsions. The cold cream or cleansing creams made up of borax- bee wax-mineral oil are water in oil in water (w/o/w) emulsions. Here globules of oil containing minute droplets of water are dispersed in oil phase. Night or lubricating creams are obtained from this by introducing super fattening agents such as Lanolin. Creams that are meant to remain on the skin for longer intervals, such as sun-tan creams, have to be so formulated that they will not penetrate the skin, whereas medical creams will have to be formulated for penetration through the skin.

It is evident that a wide variety of requirements are placed on surfactants for their use in cosmetics and detergency. A knowledge of the ways in which surfactants meet those requirements is clearly very essential for the proper development of these household and personal products.

ticles smaller than 0.05 microns, a transparent product is the result. When oil and water are mixed, the two phases will separate, but the separation can be delayed even for years with the addition of emulsifying agents. The emulsifier acts by adsorbing at the interface and thus by reducing the interfacial energy. It is the existence of this interfacial energy that is essentially responsible for the instability of an emulsion, since the large increase in interfacial area upon the formation of the emulsion droplets will cause an increase in the free energy of the system. It has also been proposed that adsorption of certain agents can momentarily produce a negative interfacial tension, a condition which is favourable for an increase in interfacial area and hence emulsification. In addition, certain emulsifying agents stabilize emulsions by causing the formation of a rather rigid interfacial film, and also by allowing the generation of electrical charge at the interface. The type of emulsion obtained can be predicted usually with the help of what is known as hydrophile-Lipophile balance (HLB). Surfactants contain both hydrophilic and hydrophobic groups and HLB values tell one about the balance of the forces due to these groups. HLB value for a surfactant can be calculated using the formula:

HLB = sum of hydrophilic group numbers —n + 7. where n is the group number for CH_2 group. Typical group numbers are given below(5) –SO-Na+, 38.7; –COO-K+, 21.1; N(tertiary amine), 9.4; —COOH, 2.1; —OH (Free), 1.9; —OH (Sorbitan ring), 0.5; —CH- or —CH_2- or CH_3-, —0.475, —(CH_2+CH_2—0)-, 0.33, —(CH_2—CH_2—CH_2—0)-, —0.15.

HLB values of selected surfactants on this basis are 40 for sodium lanryl sulfate, 20 for potassium oleate, 11.2 for sucrose monostearate, 8.4 for methanol, 7.2 for sorbitan monooleate, 3.7 for glycerol monostrearate and 1.3 for cetyl alcohol. Molecules that have a low HLB number (4 to 6) are soluble or dispersible in oil and usually give a water in oil emulsion. Those that have a high HLB value (8 to 18) on the other hand are soluble or dispersible in water and give rise to oil in water emulsion. Surfactants with HLB values in the range of 7 to 9 are commonly used as wetting agents and those with values in the range of 13 to 15 function as detergents.

Cosmetics

Cosmetics are different surfactants depending on the intended purpose of the product. Shampoo used for cleaning hair etc. is essentially a detergent solution. Even though common soap will act as a good detergent, in order that it can be effectively used also in hard water areas, synthetic detergents that are insensitive to Ca++ Mg++ etc. are most commonly used in shampoos(8). Since the public wrongly believes that lathering action is a necessary requirement for cleansing, an excessive amount of detergent is usually used. Use of such formulations unfortunately over-clean the hair, removing some of the natural fatty substances; this often makes the hair unmanageable and requires the use of what are known as conditioning agents in shampoos. These contain a number of chemicals, such as lanolin, cetyl alcohol, vegetable oils etc. Conditioners made up of cationic surfactants and, sometimes, protein-based materials are also commonly used after shampooing.

Certain products such as lipstick of course necessarily have special requirements. Firstly, none of the ingredients should be toxic. Secondly, the organic medium should disperse the pigment matter, dissolve fluoresceins, should not have any objectionable odour or taste and should have appropriate vapour pressure lest the problems of sweating, bleeding and drying out occur during the use.

Cosmetic creams are liquid or solid emulsions. The cold cream or cleansing creams made up of borax- bee wax-mineral oil are water in oil in water (w/o/w) emulsions. Here globules of oil containing minute droplets of water are dispersed in oil phase. Night or lubricating creams are obtained from this by introducing super fattening agents such as Lanolin. Creams that are meant to remain on the skin for longer intervals such as sun-tan creams, have to be so formulated that they will not penetrate the skin, whereas medical creams will have to be formulated for penetration through the skin.

It is evident that a wide variety of requirements are placed on surfactants for their use in cosmetics and detergency. A knowledge of the ways in which surfactants meet those requirements is clearly very essential for the proper development of these household and personal products.

Bibliography

1. Adamson. A. W., Physical Chemistry of Surfaces, 2nd ed., Interscience, pp 489-499 (1967).
2. Becher. P. "Theoretical aspects of emulsification, a a background for cosmetic formulation", in **American Perfumer and Cosmetics**, Vol. 77, No. 4, pp 5-9 (July 1962).
3. Carson, H. C., and Marcy, G. M., "Detergent in Household and Personal Products Industry, pp 30-34 (January 1977).
4. Davies. J. T. and Rideal, E. K., **Interfacial phenomena,** Academic Press, N.Y., pp 359-385 and 418-420 (1961).
5. Fort, T. Jr., Biilca, H. R. and Sloan, C. K., "Studies of Soiling and Detergency", Part I. Observations of naturally soiled textile fibres", **Textile Research Journal,** pp 7-12 (January 1966).
6. Fox, C., "Cosmetic Emulsions", in **Emulsions and Emulsion Technology Part II,** Ch. 13, Lissant. K. J., Ed., Dekkar, New York, 1974.
7. Harry, R. G., **Harry's Cosmeticology,** Cr. 38, Chemicol Publishing Company, New York, pp. 609-623 (1973).
8. Hollenburg, I. R., "Surface Active Materials in Cosmetics", **Drug and Cosmetic Industry,** Vol. 71, pp 42-43, and 121-124, July 1952.
9. Kravetz, L., Scharer, D. H., and Stupell H., "Formulation and Performance of Heavy Duty Liquid Detergents", Household and Personal Products Industry, pp 55-58 and 70, January 1977.
10. Ogino, K., and Agui, W., "A Study of the removal of oily soiled by rolling up in Detergency", **Bull, Chem. Soc. Japan,** Vo. 49, No. 6, pp 1703-1708 (1976).
11. Somasundaran, P. and Hanna, H. S., "Physico-Chemical Aspects of Adsorption at Solid/Liquid Interfaces, Part I, Basic Principles" in **Improved Oil Recovery by Surfactant and Polymer Flooding,** Academic Press, 1977.
12. Somasundaran, P., and Fuerstenau, D. W., "Mechanism of alkylsulfonate adsorption of the alumine-water interface" in **J. Phys. Chem., 70.** pp 90-96 (1966).
13. Stevenson, D. G., "Mechanisms of Detergency", **J. Soc. Cosmetic Chem.,** Vol. 12, No. 7. pp. 353-369 (October 1961).
14. Venkatesh, G. M., Dweltz, N. E., Madan, G. L., and Alurkar, R. H., "A study of the soiling of textiles and development of anti-soiling and soil release finishes: a review", **Textile Research Journal,** pp 352-362 (May 1974).