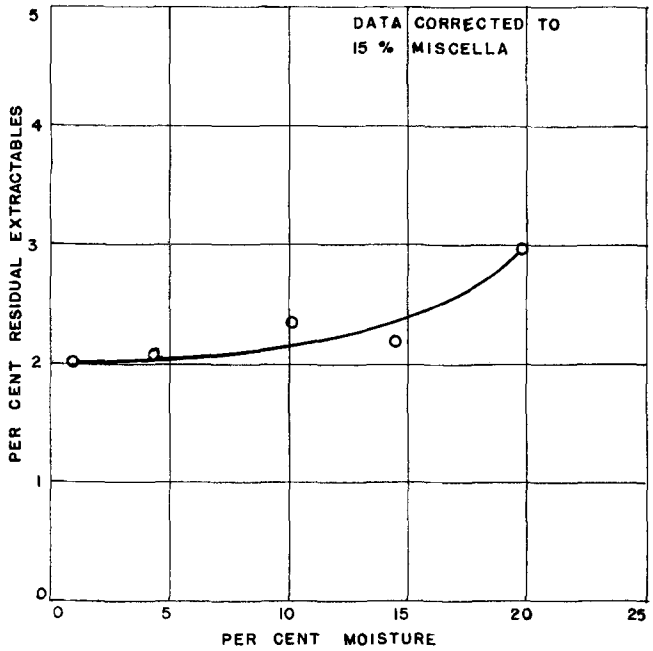

FIG. 7. Effect of moisture on residual extractables in pilot plant.
Extraction time: 26 min.
Extraction temperature: 110°F.
Residual extractables on moisture-free basis.

The extraction with hexane shows conclusively that extraction of fish meal is best carried out with trichloroethylene if as great an oil recovery as possible is to be obtained under a given set of extracting conditions. The actual difference in the results is due to the difference in the rate of solution of the oil components in the solvents, as has been suggested by Karnofsky (6).

The toxicity to cattle of certain batches of trichloroethylene-extracted soybean oil meal has raised the question of possible toxicity of other products extracted by trichloroethylene. Since the work presented in this paper was a study in extraction only, the use of trichloroethylene as an experimental solvent should not be construed as a recommendation by the authors that the product resulting from this extraction is or is not suitable as a feed.

Summary

Data are given which show the effect of the various extraction variables on the extraction of fish meal in both the laboratory and pilot plant. The use of wetting agents, although promising in the laboratory, does not appear to be of much value for pilot plant operation. A higher percentage of the oil components is removed by trichloroethylene under a given set of extracting conditions than with hexane. The mechanism of the extraction is believed to be one of surface-washing for short extractions, and for longer extractions this washing process is supplemented by diffusion.

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Adsorption of Synthetic Detergents Affects Use and Waste Disposal[1]

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DETERGENTS are members of a broad class of compounds known as "surface-active agents," so-called because they are withdrawn from water solution by surfaces of all types. The detergent molecules, attracted from the solution to the surface, orient themselves with their water-solubilizing groups directed toward the solution and the water-repellent groups toward the surface. In this way an entirely new surface is created. This surface effect, known as "adsorption," gives rise to the washing, wetting, sudsing, dispersing, and other properties associated with detergents.

In ordinary use the amount of detergent which migrates to the surface is no inconsiderable part of that which is present. It may in fact involve most of the detergent present in solution. Furthermore the detergent which becomes associated with the surface may be fixed there in a way that serves to alter the properties of the treated material even after it is removed from detergent solution.

[1] Presented at the fall meeting, American Oil Chemists' Society, Minneapolis, Minn., Oct. 11-13, 1954.

Adsorption Needs to Be Understood

This discussion is concerned with a description of the magnitude of these surface effects and with the manner in which they can be promoted or retarded, according to the particular effect which the user wishes to achieve.

The economical and effective use of detergents, especially in industry, requires a clear understanding of the effect which the detergent is intended to achieve and whether the effect is to be temporary, as in washing where it must last only until the dirt is floated away, or whether it is to be more permanent, as in textile finishes or in processes for sterilizing and mothproofing. It also requires a knowledge of the bond between the surface and the detergent. The detergent may be loosely bound so that the bulk of it can be rinsed away by fresh water; or it may be firmly bound

even to the point where chemical means are necessary to bring it back into solution. This affinity of the detergent for the surface will vary with different surface materials and with different detergents. Finally information is needed on the distribution of the detergent between the solution and the surface and the way in which this is affected by different processing conditions such as time, temperature, and concentration.

Adsorption May Be Beneficial or Harmful

The presence of the adsorbed detergent on the surface may be beneficial or it may be harmful, and the user should adjust his process to achieve the particular effect desired. For example, in paper towels a detergent is used to speed up the water absorbency. On the other hand, adsorbed detergents have a disastrous effect on writing paper. Adsorption is useful in waterproofing, in the treatment of materials that must be rewet in the removal of detergents from sewage, and in the protection of materials against bacteria and other organisms. It is generally harmful in fire fighting, in dust suppression, and in paper processing, where it interferes with sizing. At times the adsorbed detergent can be both useful and harmful. For instance, in the use of cationic detergents for sterilizing dishes and equipment it is important to have a thin film of adsorbed detergent to protect the surface against air-borne bacteria; but in the dairy industry the desorption of the cationic detergent, used to sterilize equipment, is blamed for difficulties in the cheese-making process.

Examples Show Magnitude of Adsorption

Recent advances in analytical work have provided the accuracy necessary to measure the effects of adsorption. Applications of these new methods, particularly to the processing of textiles, provide specific examples which make it easier to understand the problems encountered by the detergent user.

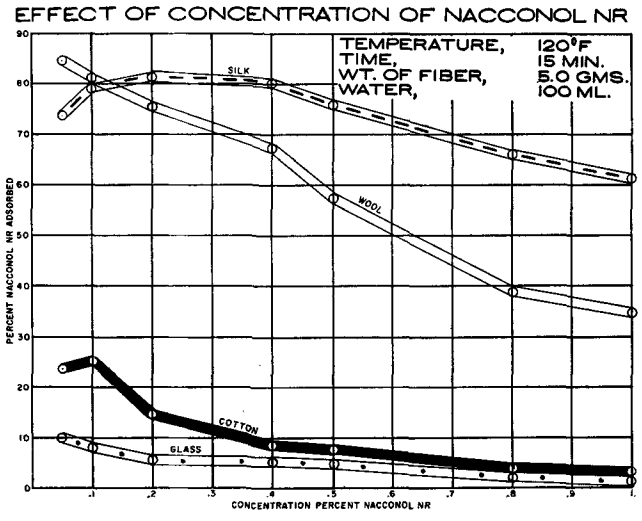

FIG. 1

Figure 1 shows the proportion of the anionic detergent, Nacconol NR,[2] withdrawn from 100 ml. of solution by 5-g. samples of different kinds of textile fibers. The anionic detergents are very satisfactory for test purposes; they are not adsorbed as actively as the usual cationic detergent would be, but they are more active in this respect than the nonionic detergents. Nacconol NR is a mixture of alkyl benzene sulfonates. The figure shows studies at concentrations, ordinarily used, ranging from 0.05-1.00%.

The great variation between the activity of different fibers or the different surfaces is immediately and strikingly apparent. It will be no surprise that wool and silk adsorb the anionic detergent most actively. At 0.1% concentration, where the detergents are frequently used for washing, the wool picks up about 80% of the detergent present in the solution within 15 min. at 120°F. Silk is similar to wool. In the case of cotton about 20% leaves the solution under the same circumstances. It does not matter whether the surface is a natural textile fiber or glass, or any other material; the depletion of the detergent solution is a very real factor. It will be seen that, at the concentrations commonly used, 5-10% of the detergent is withdrawn by glass fiber.

The amount of adsorption of anionic detergents is generally increased in acid solution. This is also true whether the material is wool or glass. Studies previously reported by Flett and Hoyt (1) showed that, under conditions used in dyeing wool, more than 98% of the detergent was transferred from the solution to the fiber. Depleted solutions can become ineffective. Under certain washing conditions a detergent can remove the soil from the wool, and then the wool can take up the detergent to the point where the soil is redeposited on the fibers.

Although the curves show the percentage of detergent adsorbed as dropping off with increasing concentrations, the actual weight of detergent adsorbed increases. For example, in the case of wool, where the amount taken up from solution decreased from 85% to 35% as the concentration was increased from 0.05 to 1.00%, the weight of detergent picked up by the wool increased over eight times.

In this test there were 20 parts of solution to one part of the fiber. This tends to conceal the surprising fact that at low concentrations the amount of detergent based on the weight of the fiber may be from five to 80 times as large as concentration of the detergent present in the solution.

Similarity Between Detergents of the Same Class

While there is a similarity in the behavior of the different anionic detergents, they can all be depended on to show variations from one another. Soap is an anionic detergent. It is less suitable for test purposes because the effects are complicated by the hydrolysis of the soap and by changes in pH. The adsorption of sodium oleate is interesting and is shown in Figure 2. It is about the same as that for Nacconol NR in the case of wool. It is quite a bit higher in the case of the cotton, possibly due to the effect of hydrolysis. It is interesting to note that, at 0.022% concentration, the cotton and wool have withdrawn the same amount of soap from solution.

Degree of Adsorption Can Be Varied by Conditions

In the use of detergents the amount adsorbed by any particular type of surface can be varied by the proper choice of operating conditions. In other words,

[2] Trademark "Nacconol" Registered U. S. Patent Office, Allied Chemical and Dye Corporation.

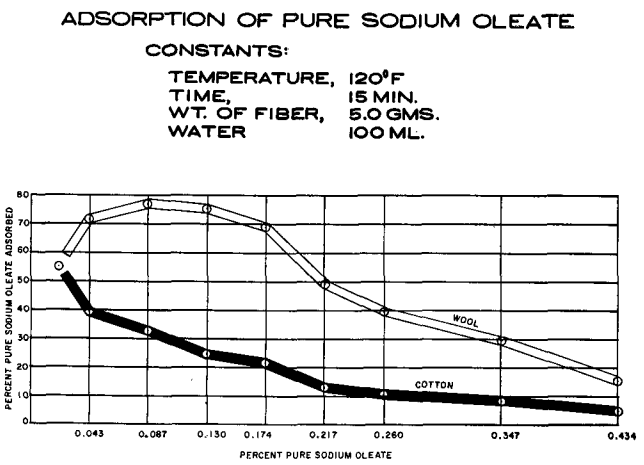

FIG. 2

adsorption can be promoted where it is desired or it can be retarded where it is objectionable. For example, adsorption is increased by longer times and reduced by shorter times, as would be expected. However where the user wishes a minimum of detergent on the surface, the times must be unexpectedly short because by far the greatest amount of adsorption takes place in the first minute. The advantage of a short time is evident in street washing, where 2 lbs. of pure detergent are used to clean a whole mile of paved city streets. This amount of detergent would be woefully inadequate if an opportunity were provided for the surfaces to pick it up. It is only possible because each part of the street is washed in the brief instant while the truck passes by.

The amount of detergent adsorbed can be increased by increasing the surface or the amount of fiber, but it should be remembered that the amount is not directly proportional to the amount of fiber.

The effect of temperature on the degree of adsorption is particularly interesting. This is shown in Figure 3. Temperature generally serves to increase

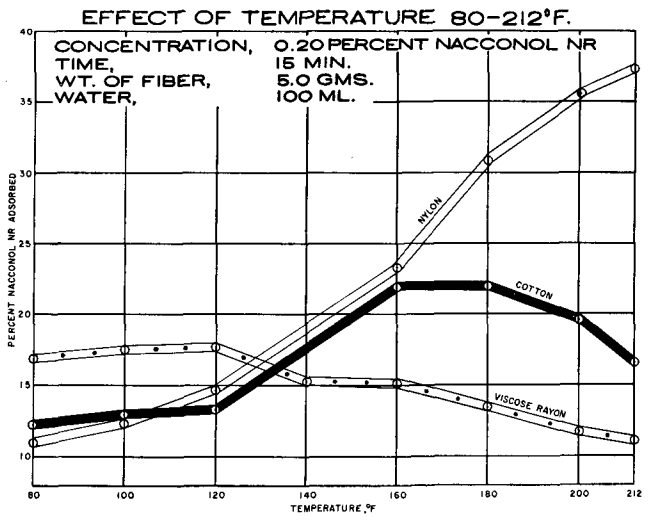

FIG. 3

adsorption up to a certain point, after which it drops off, possibly due to the detergent passing from the colloidal state into true solution or into a different type of micelle. Most interesting is the anomaly provided by nylon, where adsorption increases rapidly at higher temperatures. The study of this fiber has not been completed, and it is not certain but that the high adsorption at higher temperatures might take place at lower temperatures if a longer time were allowed. Interestingly enough, it is maintained by some nylon users that the action of detergents on nylon is slow and that where the odor of perspiration must be permanently removed from garments, prolonged soaking in detergent solution is advisable.

Adsorption in Waste Disposal

In the long run the bulk of the detergent finds its way into the waste disposal system or sewer. There is a wealth of surface and suspended matter, and the concentration of detergent is extremely low. Both of these conditions are ideal for the promotion of complete transfer of the detergent to the surface. It is safe to say from experimental data as well as from theory that the greatest part of the small traces of synthetic detergent present are adsorbed on the surfaces. Where the surface material can be settled out, it provides an easy way for removing the detergent. The remaining detergent which does not settle quickly is still fixed on the surfaces of the suspended material.

Summary

In a brief discussion such as this, it is impossible to do more than touch some of the highlights. Facts have been pointed out which serve to explain some of the many anomalies which are all too common in the use of synthetic detergents. Much progress can still be made in the economical use of detergents by a precise understanding of the surface effects required and by proper choice of materials and conditions to achieve those results.

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Editorial Note

Dr. Istvan Korpaczy of Budapest, Hungary, has called to our attention that it may not have been entirely clear in a paper entitled "A Halogenation Method for the Determination of the Total Unsaturation of Tung Oil and Eleostearic Acid" (J. Am. Oil Chemists' Soc., *30*, 417 [1953]) that L. Winkler (Zshr. f. Untersuch. Nahr. u. Genusm., *49*, 277 [1925]) first proposed the use of mercury salts to shorten the reaction time in iodine value determinations. Scotti (olii Minerali, Grassi, e Saponi, *18*, 96 [1938]) introduced the specific use of mercuric acetate in acetic acid for this purpose.

THE EDITOR.