Wool Grease from the Commercial Solvent Degreasing of Raw Wool

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Some differences between wool grease obtained by the solvent extraction of raw wool and wool grease recovered centrifugally from emulsion scour liquors are described. Refining problems arising from the peculiar properties of solvent wool grease are outlined, and some suitable refining methods are suggested.

THE CLEANSING of raw wool by treatment with organic solvents has, in the past, found only a very limited industrial application, and no literature exists on commercial solvent grease[1] as distinct from the usual grades of wool grease recovered by various methods from aqueous scour liquors.

Following the recent development by the C.S.I.R.O. of an improved method for the solvent degreasing of wool (1,2), some preliminary investigations into the refining of solvent grease have been carried out and are described in the present paper.

Effect of Recovery Method on Wool Grease Quality

The susceptibility of wool wax to oxidative degradation, particularly when it is exposed to the weather on the growing fiber, is well known. Some of the chemical changes involved in the degradation have been described (3–5), but the accompanying changes in physical properties, which have profound effects on the technology of wool grease, have not been studied. One such property is the surface activity, which increases greatly during oxidation. The increase is manifested in the ability of oxidized wool wax to form extremely stable o/w emulsions.

Greasy wool contains wool wax that varies in quality from the freshly secreted material at the fiber base to the highly oxidized material at the fiber tip. In an emulsion scour liquor, dispersed wax droplets containing a high proportion of oxidized wax are more stable than those containing mainly fresh wax, and the fresh material is preferentially separated when the emulsion is centrifuged. Centrifugal wool greases therefore contain only small proportions of the commercially undesirable oxidized wax but are obtained in low yield. Big improvements in recoveries from emulsion scour liquors are always accompanied by deterioration in grease quality.

Solvents that are suitable for the commercial degreasing of raw wool have practically no selective solvency for fresh or oxidized wool grease, and virtually all the grease is recovered. The fresh and oxidized portions are homogenized in the solution, and no opportunity exists for their recovery from the solvent as separate fractions.

Compared with a centrifugal grease recovered from an alkaline scour liquor, the color of solvent grease is dark and the acid value is high (Table I). Unlike centrifugal grease, the color darkens appreciably on storage for a few weeks or on mild heating, *e.g.*, 30 min. at 100°C.

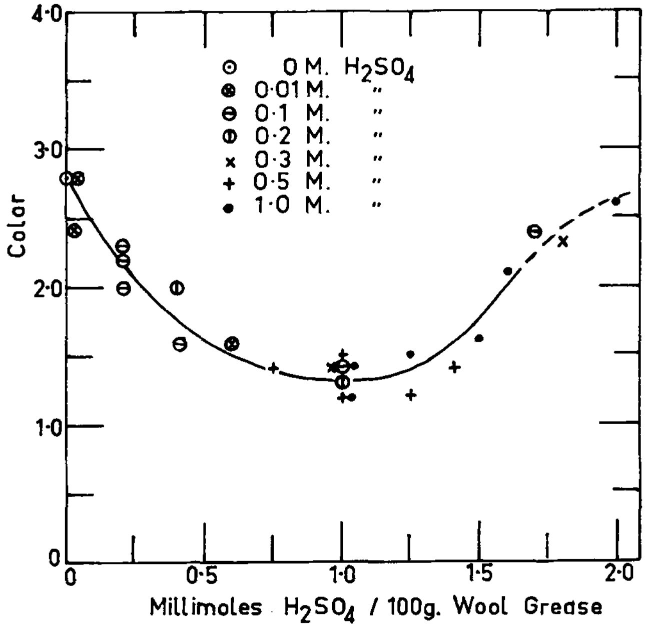

FIG. 1. Effect of acid pretreatment on peroxide bleaching. (Color scale as indicated in footnote to Table I.)

TABLE I

Typical Data for Solvent and Centrifugal Wool Greases

	Solvent	Centrifugal
Color[a]	5.7	1.3
Density (20°C.)	0.94	0.94
Total volatiles (5 hr. at 105°C.)	2.5	......
Moisture	0.5%	0.7%
Saponification value	95	110
Acid value	5.2	1.5
Unsaponifiables	47.0%	49.0%
Ash	0.25%	0.3%
Sulfur (A.S.T.M. D117-43)	Negative	Variable

[a] Red units as measured with a Lovibond Tintometer (B.D.H. pattern), using melted grease at 70°C. in a ⅛-in. cell.

The dark color, color instability, high acid value, and extreme stability of o/w emulsions of solvent grease make it more difficult to refine than centrifugal greases. Some problems which have been encountered in preliminary investigations into the refining of solvent grease are described in the following sections, and modified refining methods are suggested to overcome them. Acceptable lanolin is currently being produced commercially, using some of the suggested procedures.

Greases produced in very high yield from emulsion scour liquors are of inferior quality because they contain oxidized material. They have properties similar to those of solvent grease and should be amenable

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[1] The terms "solvent grease," "centrifugal grease," etc., will be used to describe the products obtained from the various recovery processes.

to the same refining methods. Increased production of lanolin from scour liquors should therefore be possible by modifying recovery techniques to give high yields of the inferior grease, then refining the grease by the methods developed for solvent grease.

Bleaching

Of the chemical bleaching agents tried, hydrogen peroxide was more effective than hypochlorite, chromic acid, permanganate, peracetic acid, sodium peroxide, or benzoyl peroxide. With hydrogen peroxide, good bleaching of solvent grease is only effective after pretreating the grease with mineral acid. Figure 1 shows a plot of color against quantity of acid for a series of laboratory experiments in which various pretreatments with dilute sulfuric acid were followed by a standard bleaching procedure. The method was to add dilute acid to the melted grease (100 g.) at 85°C., stir vigorously for a few minutes, then add 35% hydrogen peroxide (3.0 ml.) and bleach for 30 min. at 85°C. The color of the bleached product was measured after washing with 100 ml. of water and drying.

The optimum quantity of sulfuric acid is about 10^{-3} moles per 100 g. of grease; the effect of the acid is independent of its concentration up to 1M. At concentrations higher than 1M, the acid tended to react with the solvent grease to give a darker color. With larger quantities of dilute acid, the acid treatment gave a small improvement in grease color, but the effectiveness of the subsequent bleach was reduced. In the same range of conditions the bleaching of a centrifugal grease was unaffected by acid quantity.

The most economical quantity of hydrogen peroxide is about 3 ml. of 35% reagent per 100 g. of grease. Smaller quantities cause much less bleaching; larger quantities give very little additional improvement. No advantage was found in using equivalent quantities of weaker (27.5%) or stronger (up to 88%) peroxide.

Bleaching by this method causes an increase of 1–2 in the acid value of the grease. The color produced is equal to that of refined centrifugal lanolin of a fair quality.

Color Stabilization

Darkening of wool grease takes place in two stages, first the formation of oxidized material, second the conversion of oxidized material to dark compounds. Removal of oxidized material therefore produces only a temporary color stability; as soon as further oxidation takes place, more color-producing compounds are formed. To produce permanent color stability it is necessary either to prevent the darkening reaction from taking place or to remove not only the color-forming compounds but also the wool grease fraction that can oxidize to color-forming compounds.

Treatment with sodium bisulphite was found to confer excellent color stability, which suggests that aldehydes or ketones play an important part in darkening reactions. Optimum treatment conditions were saturated sodium bisulphite solution (2 ml.) added to the melted grease (100 g.) at 70°C. and agitated for 5 min. The grease was then washed with water. Unfortunately the product again developed color instability after peroxide bleaching, and the bisulphite became bound into the grease, producing an unacceptably high ash content.

Extraction of solvent grease with methanol at room temperature removed in solution about 12% of the grease, including all the color-forming compounds, but the insoluble fraction again developed color instability on peroxide bleaching.

Neutralization of the grease by treatment with aqueous alkali and recovery of the grease by centrifuging gave a color-stable product which remained color-stable after peroxide bleaching (see below).

Neutralization

The emulsion formed when solvent grease is neutralized by the addition of aqueous alkali fractionates in the same way as an emulsion scour liquor when passed through a centrifuge. The undesirable oxidized fraction does not separate, and the recovered grease has excellent color stability and a paler color than the starting material. Yields from the neutralizing process are therefore lower with solvent grease than with centrifugal grease, which has already undergone the fractionation in the primary recovery process. Yields of 75%–85% are usual, and the desirable properties of the neutralized product are retained up to 90% yield.

Neutralization of peroxide-bleached solvent grease with sodium hydroxide solutions is always accompanied by a slight darkening in color. Boiling the neutralized grease with dilute mineral acid restores the original color and gives an increase of 0.6 in the acid value. Reneutralization once more causes the color to appear. The color is not removed by prolonged extraction of the grease with boiling water or of an ether solution of the grease with 2:1 water/ethanol. These observations suggest the presence in peroxide-bleached grease of a pale organic acid which forms a dark sodium salt insoluble in water or water/ethanol.

As neutralization of unbleached solvent grease is not accompanied by the same phenomenon, it is presumed that the organic acid involved is formed during the bleaching process. If, as seems probable, it is a normal constituent of bleached solvent grease, it will be impossible, by the methods described here, to obtain a soap-free, bleached solvent grease with an acid value below 0.6.

Attempts to remove the free organic acids by complexing with urea as suggested by Truter (6) were unsuccessful.

Reduction in Ash Content

Crude solvent grease has an ash content of about 0.25%, and normal refining operations reduce this figure to less than 0.1%. Further reductions, or reductions independent of other refining operations, can be achieved by boiling with dilute sulfuric acid and settling. For example: a) solvent grease, ash content 0.24%, boiled with half its volume of 1% sulfuric acid and settled, gave a grease with 0.04% ash and a slightly improved color; b) under similar conditions the ash content of a neutralized solvent grease was reduced from 0.12% to 0.04% with a slight color improvement. Such treatments increase the acid value of the grease by about 1.0.

Deodorizing

Solvent grease produced commercially by the C.S.I.R.O. process normally contains 1.5%–2.5% of residual solvent. This represents higher boiling material from the petroleum solvent used, which has a boiling range of 150°–200°C.

The odor associated with the residual solvent can be removed by steam stripping in a conventional stripping column to a residual solvent content of 0.1% or less.

Sulfur Content

Tests in accordance with A.S.T.M. method D117-43 have always shown that solvent grease is sulfur-free. Some discoloration of the copper strip usually occurs, but sulfur cannot be detected in the discolored film.

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[Received March 3, 1960]

Analysis of Mixtures of Ionic and Nonionic Surface-Active Agents. Separation and Recovery of Components by Batch Ion Exchange[1]

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Mixtures of anionic and nonionic surfactants or cationic and nonionic surfactants can be separated by stirring an aqueous solution of the mixture with a small amount of a strong anion exchange or strong cation exchange resin, respectively. The resin-ionic surfactant complex is removed by filtration and washed; the nonionics are recovered from the filtrate and washings.

By suitable treatment the ionic surfactants can be removed selectively from the resin. In the case of anionic surfactants, soaps, alkyl sulfates, and alkylaryl sulfonates can successively be removed from the resin; with cationics, nonquaternary and quaternary surfactants can be selectively removed. Results obtained with various mixtures of surface-active agents are discussed.

A NUMBER of years ago the separation of nonionic surface-active agents from mixtures with anionics by ion exchange resins, using a batch technique rather than the usual column method, was described (1). In this batch method an aqueous solution or dispersion of the surfactant mixture was stirred with a relatively small amount of an anion exchange resin, which complexed the anionic surfactants without removing any of the nonionic material. After the anion exchange resin with its complexed anionic surfactant had been removed by filtration and washed well with alcohol, the nonionic was recovered from the filtrate and washings. Results obtained with 14 binary mixtures of nonionics and anionics, representing all the major types available commercially, showed that the nonionic could be recovered in substantially quantitative yield by this method.

In the present paper the method has been extended to the separation of nonionics from their mixtures with cationics and, even more significantly, to the separation and recovery of the anionics and cationics complexed with the ion exchange resin.

Experimental

Separation of Nonionics from Their Mixtures with Cationics. Four to five grams of the surfactant mixture, dissolved or dispersed in 100 ml. of distilled water, are stirred for 4–5 hrs. with 20 g. of purified, 200–400 mesh, Dowex 50-X4 acid form cation exchange resin,[2] maintaining the mixture acid to Congo red during the stirring period by the addition of dilute hydrochloric acid, if necessary. (The Dowex 50-X4 resin is purified by stirring it for 15 min. with methanol, at least twice, until a colorless filtrate is obtained.)

TABLE I

Separation and Recovery of Nonionics from Mixtures with Cationics

No. Mixture (wt.)[a]	Nonionic Product			
	Yield	n_D^{25}		Cationic test[b]
		Obsd.	Theor.	
1. Pluronic L62 (1.04 g.) Ethomene C/25 (1.32 g.) Arquad 2HT (1.28 g.)	98% (1.02 g.)	1.4534	1.4540	—
2. Brij 30 (1.61 g.) Amine 220 (1.53 g.) Cationic SP (1.77 g.)	99% (1.59 g.)	1.4531	1.4520	—
3. Igepal CO-710 (2.20 g.) Armeen SD (2.19 g.) BTC (2.02 g.)	103% (2.27 g.)	1.4847	1.4842	—

[a] 100% actives basis.

[b] Kortlandt, C., and Dammers, H.F., J. Am. Oil Chemists' Soc., *32*, 58 (1955).

After the surfactant mixture is stirred with the resin for 4–5 hrs., it is filtered, and the resin is washed well with 95% ethanol. The nonionic material in the filtrate and washings is obtained by neutralizing the filtrate and washings to phenolphthalein with dilute sodium hydroxide, evaporating them to dryness, and extracting the residue with acetone to separate it from the inorganic salts. After removal of the acetone on the steam bath, the residue is dried briefly in the oven at 110°C. and is weighed.

Results obtained by use of this method are given in Table I. The results are comparable to those obtained previously for the separation of nonionics from their mixtures with anionics, using anion exchange resins in a batch procedure (1). The nonionic is recovered in substantially quantitative yield and is of good purity, as evidenced by the negative results

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[1] Presented at the 51st fall meeting, American Oil Chemists' Society, New York, October 17–19, 1960.

[2] Dow Chemical Company, Midland, Mich.