Bleaching of Wool Grease

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Abstract

Bleaching tests on three dark wool greases show that, among many systems tested, only hydrogen peroxide and sodium chlorite have significant effects. Pale greases are obtained by adding controlled amounts of sulphuric acid, phosphoric acid, or sodium phosphate with the hydrogen peroxide; sulphuric acid and phosphoric acid improve the bleaching power of sodium chlorite.

Introduction

UNTIL RECENTLY, wool was scoured mainly in solutions of soap and sodium carbonate, and wool grease of good quality could be obtained by using the centrifugal recovery process (1). Although there was some variation in the quality of the grease, mainly depending on wool quality and recovery efficiency, refining by bleaching with hydrogen peroxide was usually successful (2). Neutralization of the grease to meet various specifications was also easy as the initial free fatty acid was seldom above 2%, and the neutralized grease readily separated from the aqueous phase.

However, in many plants, soap has been replaced by synthetic detergents, especially of the nonionic type, and the recovered greases are darker than those from soap scouring (3,4) and are more difficult to bleach. Wool grease obtained by solvent extraction of wool is also darker and more difficult to bleach than centrifugal grease (5).

In this paper, the effects of aqueous bleaching agents on the color of dark greases from commercial nonionic detergent scour liquors and from the C.S.I.R.O. solvent degreasing process (6) are reported. As there are many agents for which bleaching potential is claimed, preliminary tests were done to find the more promising systems, which were then investigated more thoroughly.

Experimental and Results

Bleaching Technique. The bleaching solution was added to the crude grease (25 g) and vigorously stirred with a constant speed stainless steel stirrer for 1 hr at 95C. Water (25 ml) was then added and the resultant emulsion stirred for a further 15 min. The grease and aqueous phases were separated by centrifuging the emulsion at 70C for 30 min. The color of the separated grease was measured in a Lovibond Tintometer using a $1/8''$ cell.

TABLE I

Bleaching Systems Used in Preliminary Tests

Calgon (sodium hexametaphosphate)
Calgon + sulphuric acid
Calgon + nitric acid
Calcium chloride
Chromium trioxide + sulphuric acid
Ethylenediamine tetra-acetic acid
Formaldehyde
Hydrogen peroxide
Hydrogen peroxide + Calgon
Hydrogen peroxide + chromium trioxide
Hydrogen peroxide + ethylenediamine tetra-acetic acid
Hydrogen peroxide + sulphuric acid
Hydrogen peroxide + trisodium phosphate
Hypophosphorous acid
Peracetic acid
Peracetic acid + Calgon
Peracetic acid + phosphoric acid
Peracetic acid + sulphuric acid
Perchloric acid
Phosphoric acid
Potassium dichromate + sulphuric acid
Potassium persulphate + sulphuric acid
Potassium persulphate
Sodium bisulphite + formaldehyde

Sodium bisulphite
Sodium borate
Sodium borate + Calgon
Sodium chlorite
Sodium chlorite + Calgon
Sodium chlorite + formic acid
Sodium chlorite + hydrochloric acid
Sodium chlorite + phosphoric acid
Sodium chlorite + sulphuric acid
Sodium hydrosulphite
Urea
Zinc dust
Zinc dust + acetic acid
Zinc dust + sulphuric acid

Bleaching systems used under various conditions in the initial tests are shown in Table I.

Although almost all these systems improved the color of dark wool grease, only those containing hydrogen peroxide or sodium chlorite with various additives were sufficiently promising to warrant further investigation.

As some greases can be bleached more easily than others, the following tests were carried out with three greases, which represent some of the dark greases likely to be encountered in commercial practice. They were obtained from (a) solvent degreasing of wool, (b) neutral nonionic scouring of dags wool; afterwards referred to as Grease A and (c) neutral nonionic scouring of Merino 64s fleece wool: Grease B.

Bleaching with Hydrogen Peroxide. All experiments were carried out using 130 vol. (35% w/w) hydrogen peroxide solutions. Figure 1 shows that small amounts (less than 1 ml/100 g) of hydrogen peroxide rapidly reduce the grease color, but further additions have a smaller effect. With the two darker greases, it is clear that large amounts of hydrogen peroxide will be required to reduce the color to less than 0.6 red units. (In this paper, greases with color less than 0.6 red units are considered to be of high quality.) Although the bleaching conditions were varied, better colors could not be obtained and, with solvent grease, increased reaction times darkened the grease again. Generally, the maximum bleaching effect was obtained by adding the hydrogen peroxide slowly to the grease at 65C, raising the temperature to 90C and stirring vigorously for 30 min. On a large scale, greater stirring times may be necessary to ensure adequate contact between grease and hydrogen peroxide.

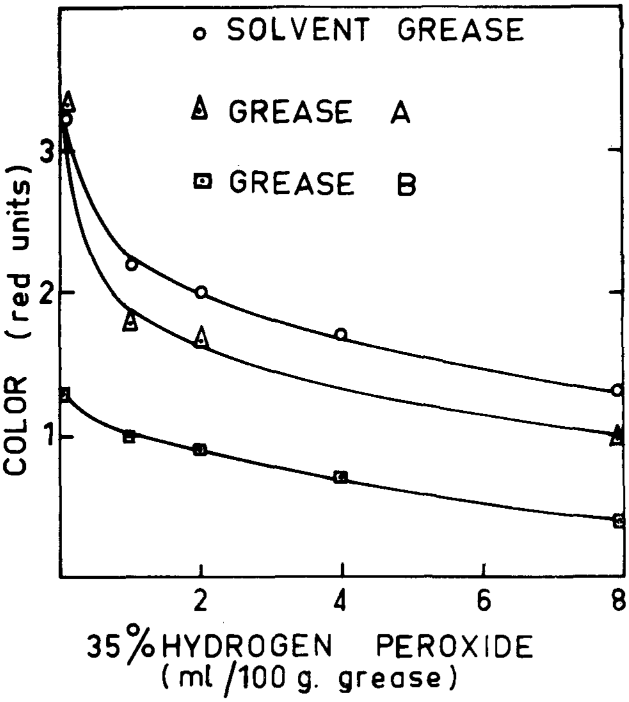

FIG. 1. The effect of hydrogen peroxide on the color of wool greases.

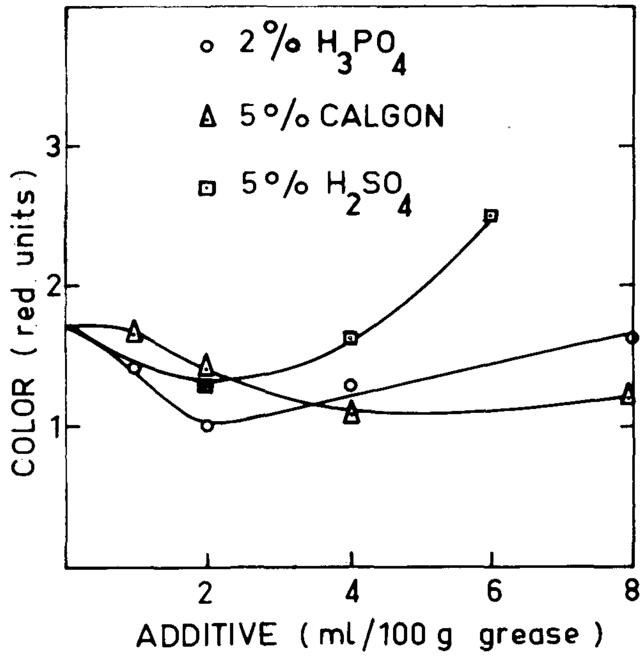

FIG. 2. The effect of additives on hydrogen peroxide (4 ml/100 g grease) bleaching of solvent grease.

To increase the effect of hydrogen peroxide, various quantities of the following substances were added to the bleaching system or were used to pretreat the grease before bleaching: urea, ethylenediamine tetraacetic acid, nitric acid, ammonium hydroxide, sodium hydroxide, sodium chlorite, sulphuric acid, phosphoric acid, and various sodium phosphates.

Within certain limits of concentration, the last three increased the effect of hydrogen peroxide on some of the greases. However, at economical concentrations of peroxide (4 ml/100 g grease), the best colors obtainable are 1.0, 0.8, and 0.6 red units for solvent grease, Grease A, and Grease B, respectively (Figs. 2, 3, and 4). Hydrogen peroxide alone, or in the presence of additives, is therefore unsuitable for refining dark greases to high quality lanolin.

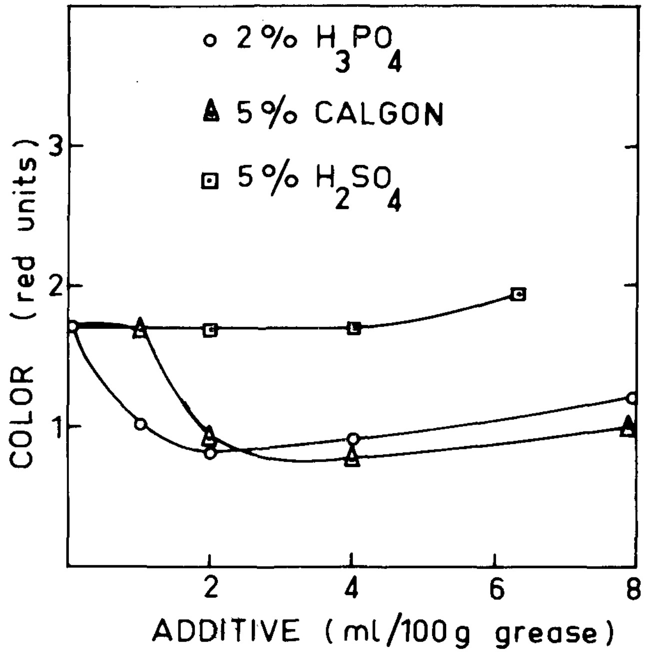

FIG. 3. The effect of additives on hydrogen peroxide (4 ml/100 g grease) bleaching of grease A.

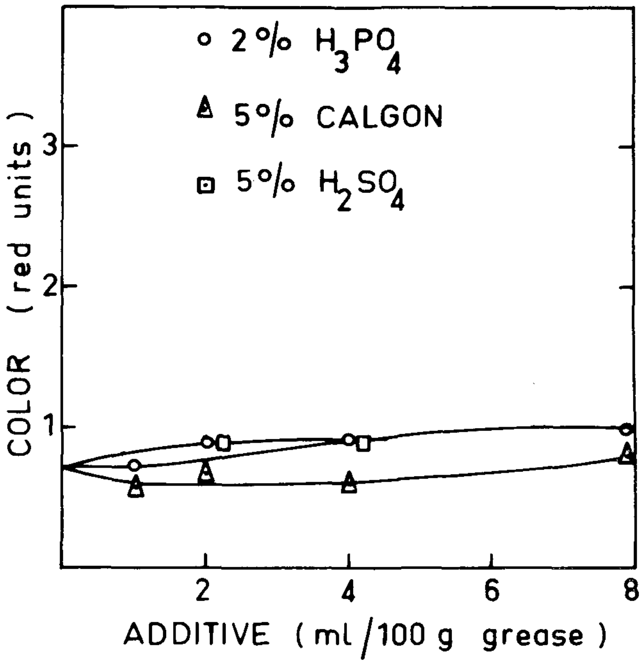

FIG. 4. The effect of additives on hydrogen peroxide (4 ml/100 g grease) bleaching of grease B.

From the bleaching results with hydrogen peroxide, two conclusions can be drawn: (a) No definite procedure can be given to cover peroxide bleaching of all greases; systems that work well with one grease may have only a slight effect on others. (b) High quality greases cannot be produced economically by bleaching the darker greases with hydrogen peroxide.

On a commercial scale, moderate bleaches of dark greases can usually be obtained by (a) 2.0 ml of 5% Calgon + 4 ml of 35% H_2O_2 per 100 g grease; (b) 2.0 ml of 1% H_3PO_4 + 4.0 ml of 35% H_2O_2; or (c) 2.0 ml of 5% H_2SO_4 + 4.0 ml of 35% H_2O_2. Preferably the bleaching reaction should be carried out in stainless steel vessels although wood, stoneware, glass, or plastic lined equipment may be used. Valves, gaskets, and pipelines of polyvinyl chloride or polyethylene plastics are suitable.

Bleaching with Sodium Chlorite. A solution of commercial grade sodium chlorite (85% active) was

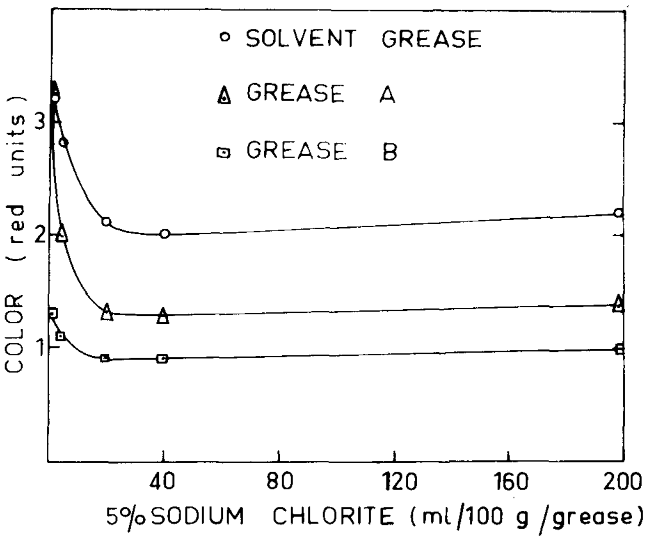

FIG. 5. The effect of sodium chlorite on grease color. Reaction time, 30 min; bleaching temp 95C.

TABLE II

The Effect of Reaction Time and Temperature on Bleaching with 10% Sodium Chlorite (40 ml/100 g grease) + 5% Phosphoric Acid (20 ml/100 g grease)

Grease	Color of bleached grease (red units)							
	Reaction time (min) at 95C				Reaction time at 65C			
	15	60	120	240	15	30	60	120
Solvent	0.5	0.5	0.5	0.7	0.6	0.6	0.7	0.7
Centrifugal A	0.5	0.4	0.4	0.5	0.6	0.5	0.5	0.5
Centrifugal B	0.4	0.4	0.3	0.4	0.3	0.4	0.3	0.4

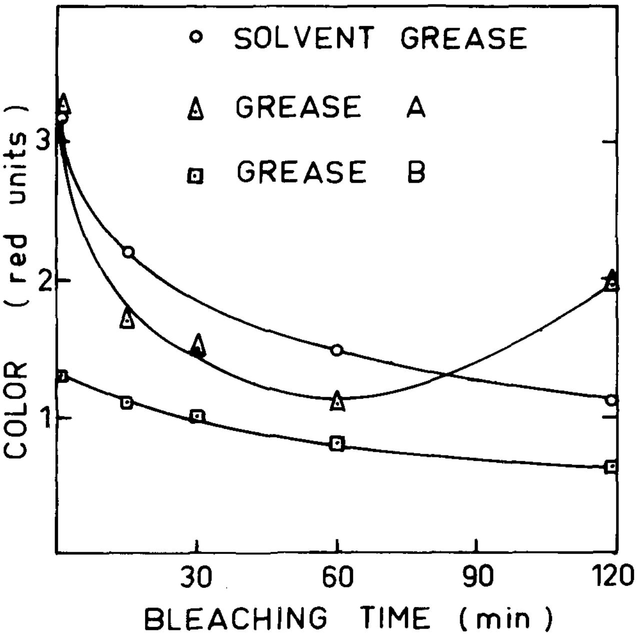

Fig. 6. The effect of time on bleaching with 10% sodium chlorite (100 ml/100 g grease) at 95C.

used in the bleaching experiments. In small concentrations, sodium chlorite has a marked effect on the color of the three greases (Fig. 5). However, with increasing concentration of sodium chlorite, bleaching efficiency decreases and the color reaches a limiting value. The colors of Greases A and B were improved by increasing the bleaching time up to 2 hr (Fig. 6), but further increases gave a darker product. With solvent grease the maximum bleaching effect occurred after 1 hr. Variations in bleaching temperature between 65C and 95C had no effect.

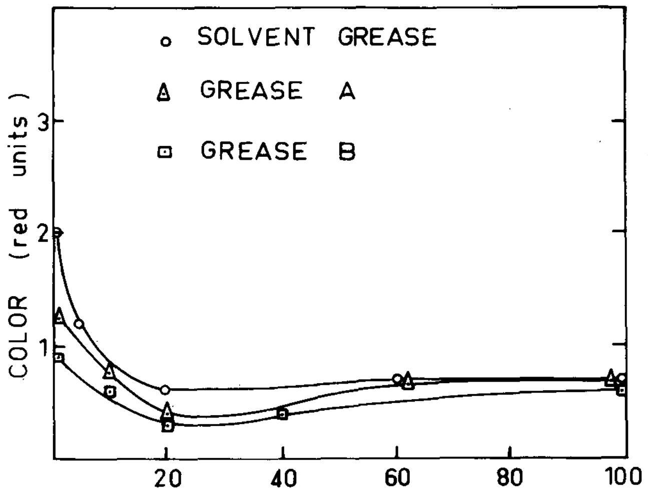

Fig. 7. The effect of 10% sodium chlorite (40 ml/100 g grease) + phosphoric acid on grease color.

The bleaching effect of sodium chlorite is improved in the presence of mineral acids, and a color of 0.6 red unit was obtained from the darkest grease. The effect of 10% sodium chlorite (40 ml/100 g grease) and varying quantities of 5% (v/v) phosphoric acid at 95C for 30 min is shown in Figure 7. Maximum bleaching occurs at an acid concentration of 20 ml/100 g grease; above and below this concentration, the bleaching effect diminishes. Similarly, at other concentrations of sodium chlorite, there is an optimum concentration of phosphoric acid. For maximum bleaching, however, sodium chlorite (40 ml/100 g grease) and phosphoric acid (20 ml/100 g grease) should be used.

An advantage of the sodium chlorite + phosphoric acid system is that bleaching times and temperatures are not critical. For temperatures between 65C and 95C, and for times between 15 min and 2 hr there is little change in grease color (Table II).

When slightly darker greases can be tolerated, bleaching can be carried out with smaller quantities of sodium chlorite or by using sulphuric acid in place of phosphoric acid. Typical results for these systems are shown in Table III.

Commercial Bleaching with Sodium Chlorite. In practice, dark wool greases from centrifugal recovery processes or from solvent degreasing should be bleached as follows: wool grease (1 T) is melted at 70C and 5% (v/v) phosphoric acid (45 gal) is added with vigorous stirring. After 10 min, 10% (w/v) sodium chlorite (88 gal) is added and stirred vigorously for 30 min. The resulting emulsion is washed in an equal quantity of water at 80–100C for 30 min and then centrifuged to recover the bleached grease.

For moderate bleaches of solvent grease or when moderate color centrifugal greases are to be bleached, the amount of 5% phosphoric acid should be reduced to 9 gal and the amount of 10% sodium chlorite reduced to 25 gal per ton of grease.

With the best grades of centrifugal grease, sodium chlorite + acid and hydrogen peroxide are equally effective for bleaching. For economic reasons the latter should be used.

Color Stability of Bleached Greases. As oxidized wool greases darken when heated, it might be expected that the heat stability of greases would be affected by the peroxide and chlorite bleaching processes. However, the darkening rates of solvent grease and Grease B were not significantly increased after

TABLE III

The Bleaching Effect of Sodium Chlorite and Acid on Wool Greases

Bleaching conditions (100 g grease)	Grease color (red units)		
	Solvent grease	Grease A	Grease B
10% NaClO$_2$ (20 ml); 5% H$_3$PO$_4$ (4 ml); 95C; 30 min	1.0	0.5	0.6
10% NaClO$_2$ (40 ml); 5% H$_2$SO$_4$ (8 ml); 95C; 30 min	0.8	0.7	0.4

TABLE IV
The Effect of Heating on Grease Color

Bleaching treatment (100 g grease)	Color increase (red units) after various heating times at 100C					
	Solvent		Grease A		Grease B	
	4 hr	16 hr	4 hr	16 hr	4 hr	16 hr
None	0.3	1.1	0.1	0.6	0.1	0.1
5% H_2SO_4 (2 ml) + 35% H_2O_2 (4 ml)	0.3	1.0	0.3	0.9	0.2	0.2
1% H_3PO_4 (4 ml) + 35% H_2O_2 (4 ml)	0.1	0.4	0.2	0.3	0.1	0.1
5% Calgon (8 ml) + 35% H_2O_2 (4 ml)	0.3	0.7	0.2	0.4	0.1	0.2
5% H_3PO_4 (20 ml) + 10% $NaClO_2$ (40 ml)	0.2	0.7	0.3	0.7	0.4	0.6
5% H_3PO_4 (4 ml) + 10% $NaClO_2$ (20 ml)	0.2	0.5	0.3	0.6	0.1	0.2

bleaching with hydrogen peroxide or sodium chlorite (Table IV). With the higher concentrations of sodium chlorite, the darkening rate of Grease A was increased, but as this system is not recommended, the effect has little practical importance.

ACKNOWLEDGMENT
Bleaching experiments were carried out by Miss B. A. Murray.

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[Received September 4, 1962—Accepted November 26, 1962]

A Comparison of the Effects of the Polyunsaturated Fatty Acids of Cuttlefish Liver Oil and Cottonseed Oil on Cholesterol Metabolism

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Abstract

Rats fed ad lib. for 12 weeks either a fat-free diet, a diet containing 15% cottonseed oil, or a diet containing 15% cuttlefish liver oil, with or without exogenous (1%) cholesterol, were studied to evaluate and compare the effect of polyunsaturated fatty acids of cuttlefish liver oil and cottonseed oil on cholesterol metabolism. The results indicate that the longer chain polyunsaturated fatty acids contained in the fish oil cannot substitute for the essential fatty acid, linoleic, either as far as effect on various aspects of cholesterol metabolism are concerned or in the ability to form arachidonic acid. The observed interference of cuttlefish liver oil with the absorption of exogenous cholesterol may be caused by the presence in this oil of the highly unsaturated long chain fatty acids.

Introduction

THE HYPOCHOLESTEROLEMIC effect of vegetable oil has been ascribed to its high polyunsaturated fatty acid content, which, in most vegetable oils consists primarily of the essential fatty acid linoleic acid. Recently investigators have reported hypocholesterolemic activity in fish oils which, although high in polyunsaturated fatty acid, are relatively low in essential fatty acids. Ahrens et al. (1) fed a diet containing 40% menhaden oil (4% essential fatty acids) to two patients, one with hyperlipemia and the other with hypercholesterolemia and found that there was a continued depression of the serum levels of cholesterol, phospholipids, and triglycerides. They concluded that the observed effects on serum lipid levels were unrelated to the essential fatty acid and sterol content of the dietary fats. Other investigators (2,3,4) obtained similar serum cholesterol-depressing effects with various fish oils, and concluded that there was no basis for the suggestion that elevated serum cholesterol levels resulted from an essential fatty acid deficiency.

The investigation was undertaken in order to evaluate these observations and to determine the effects of the polyunsaturated fatty acids in a fish oil, as compared with the linoleic acid contained in cottonseed oil, on some aspects of cholesterol metabolism.

Cuttlefish are common in the Japanese diet, and cuttlefish liver oil from the liver of *Ommastrephes sloani pacificus,* in addition to its commercial uses, is considered an edible oil (obtained from Nippon Kagaku Shiryo Co., Japan). The cuttlefish liver oil used in this investigation had an iodine value of 193 whereas the cottonseed oil had an iodine value of 115. The fatty acid composition of cuttlefish liver oil compared with that of cottonseed oil (determined by gas-liquid chromatography) is shown in Table I. The major differences between these two oils are in the linoleic acid content (cottonseed oil contains 44.7% linoleic acid compared with 1.4% linoleic acid in cuttlefish liver oil) and in the large quantities of longer chain length polyunsaturated fatty acids found in cuttlefish liver oil and not in cottonseed oil.

Experimental

Weanling albino male rats of the U.S.C. strain were divided into groups of 12 each and were fed the following diets: Group I, a fat-free diet (FF); Group II, a diet containing 15% cottonseed oil (CSO);

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