# ✗The Dual-Solvent Extraction of Wool Grease with Hexane and Aqueous Isopropanol

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## ABSTRACT

Hexane solutions of three wool greases of different purities—(a) B.P. grade, (b) a typical commercial grade, and (c) a very crude grease— were extracted by countercurrent flow of aqueous isopropanol (60% v/v IPA) in a 12-stage mixer-settler pilot plant. Fractionation performance was in close agreement with that predicted by an extraction model developed previously. Concentrations of detergent in the product greases were 0.00%, 0.00% and 0.43%, respectively. However, even with the crude grease the concentration of detergent oligomers with more than 7 ethoxylate units was zero; free acids content was slightly reduced; and the free cholesterol content was unaffected. The color of the wool grease was improved by solvent extraction, but the bleachability was only marginally improved. The complete removal of detergent oligomers indicates that the extraction technique will improve the water-emulsifying capacity of certain wool greases and overcome the synergism responsible for hypersensitivity.

## INTRODUCTION

Crude wool grease must be refined for use in pharmaceuticals, to conform to the requirements of various pharmacopoeia (1). These include specifications for the maximum allowable content of free fatty acids, moisture and ash. In some applications, the concentration of free alcohols and detergent are particularly important because clinical studies have shown that, when both are present, some synergism of hypersensitivity occurs (2). The presence of detergent has also been shown to reduce the water-absorbing or emulsifying characteristics of wool grease (3).

Detergent, free alcohols and free acids have been removed from either molten wool grease or a solution of wool grease in a nonpolar solvent by extraction with a suitable polar solvent (3-6). However, continuous multistage extraction was not achieved because suitable equilibrium data and a design procedure for the multicomponent wool-grease system were not available.

Recently, countercurrent solvent extraction with hexane and aqueous isopropanol (60% v/v), as the nonpolar and polar solvents, respectively, has been shown to achieve useful separations of detergents and free acids from wool grease (7). Subsequently, a strategy was developed which enabled the equilibrium distribution of wool-grease components between these solvents to be specified in a manner suitable for equipment design (8), and a multicomponent model for the design of dual-solvent extraction systems was developed (9). Dual-solvent extraction was selected for refining wool grease because the use of a center feed (as in fractional distillation) enables both the removal of a particular component (e.g., detergent) from the nonpolar solvent, and the loss of another component (e.g., ester) in the polar solvent to be specified. The predicted removal of detergent and loss of ester from a 4-component mixture representing wool grease was experimentally confirmed using a mixer-settler pilot plant (10).

To test the practical applicability of the above results, 3 different commercial wool greases were extracted in a 12-stage mixer-settler pilot plant. Based on the results of studies with the multicomponent design method (9), stage 5 was selected as the feed point. The results of the three extraction runs are discussed in this paper. For two greases, bleaching experiments were performed before and after extraction to assess the effect on bleachability.
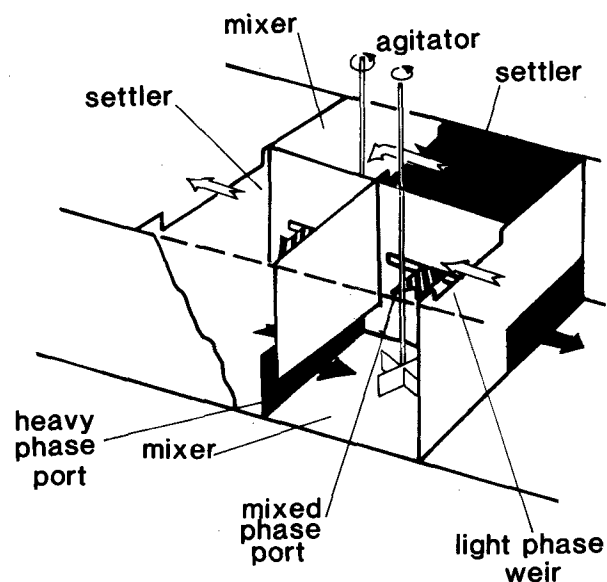
## EXPERIMENTAL

### Equipment

The 12-stage mixer-settler cascade consisted of a box divded by partitions into a series of alternate mixing and settling compartments (Fig. 1), based on principles set down by Williams et al. (11).

The two phases were brought into intimate contact in the mixing compartment and passed together as an unstable emulsion to the settler through the mixed-phase port. In the settler, the phases separated; the heavy phase (IPA-rich) passed on to the mixer of the next stage through a port placed low in the wall, while the lighter phase passed over an open weir to the next adjacent mixer in the opposite direction.

A flow diagram for the mixer-settler and auxiliaries is shown in Figure 2. The hexane and aqueous IPA solvents were pumped from storage by magnetically coupled gearpumps (P1, P2) via miniature needle valves (V1, V2) and rotameters (R1, R2) to the cascade. Hexane feed and product were stored in 20-L stainless-steel containers. Aqueous IPA feed and product were stored in 25-L polyethylene containers. The central feed, containing wool grease in hexane solution, was pumped from a calibrated glass feed tank by a magnetically coupled gear pump (P3) through a miniature needle valve (V3) and rotameter (R3) to the mixing compartment of stage 5.

The levels of the interfaces in the settling compartments were determined by the height of the mixed-phase port and the volume fraction of the aqueous phase in the mixer, except in compartment 1 where the heavy phase was discharged; in this alone, the level was controlled externally by a needle valve (V4).



⟩⟩ light phase (hexane-rich phase)

⟩⟩ heavy phase (IPA-rich phase)

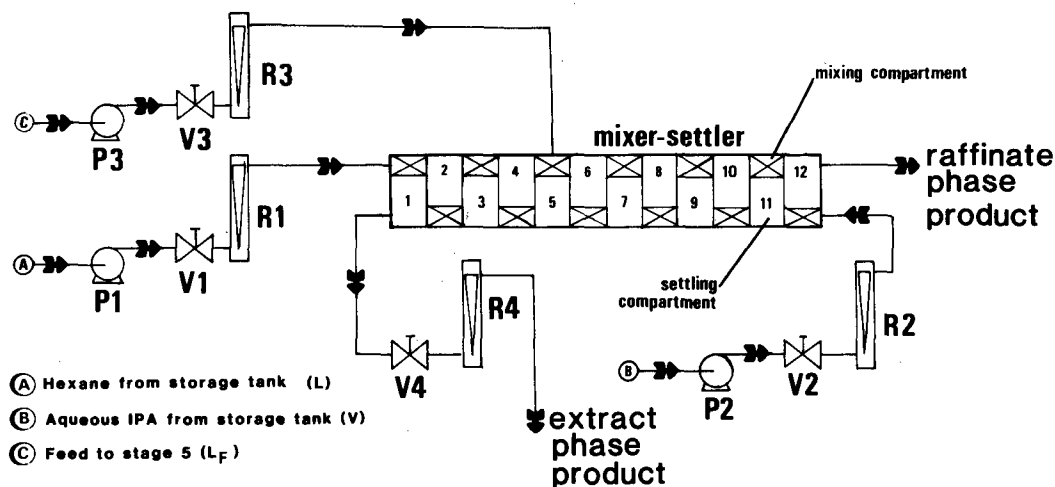FIG. 1. Arrangement of mixers and settlers.

FIG. 2. Flow diagram for mixer-settler pilot plant.

An inherent advantage of the mixer-settler as an experimental tool is the ease with which samples of the phases may be withdrawn from each stage. Samples were withdrawn using a "Manostat" syringe inserted through a hole (2 mm diameter) drilled in the lid of the settler. A small wad of plasticene was used to seal the hole. Complete details of construction are given elsewhere (10).

## Reagents

The characteristics of the three wool greases used as feeds are given in Table I.

Grease A (supplied by Croda Chemicals Group, Victoria) was a high-quality product obtained from grease recovered from wool-scouring liquors, in which soap and sodium carbonate were the scouring agents. Detergent (1.96% w/w, Lissapol TN450) was added to this grease to provide an initial test of the capabilities of solvent extraction as a removal process.

Grease B, a typical commercial quality product, was recovered from the conventional scouring of a locks, pieces and crutchings blend of merino wool at a commercial scouring plant (Dodd and Co., Melbourne).

Grease C, a crude product characterized by a very high detergent content (>3.09% w/w), was recovered from the Lo-flo scouring of a merino fleece wool (12).

The detergent added to wool grease A and used in the scouring liquors from which greases B and C were recovered was a nonyl-phenol/ethylene oxide condensate with ca. 8 ethoxylate units in the chain (Lissapol TN450, supplied by ICI, Australia).

The solvent phases were prepared from distilled water and laboratory-grade solvents as follows. Equal volumes of hexane and aqueous isopropanol (60% v/v IPA) were equilibrated to yield a raffinate phase rich in hexane and an extract phase rich in IPA. The wool-grease feed solutions (30 L for each extraction) were prepared as 10% w/v solutions of grease in raffinate solvent. Saturated phases were used to minimize solvent miscibility during extraction runs.

All solvents and chemicals for analytical methods were of analytical reagent grade (8).

## Procedure

To commence a run, the mixer-settler was filled to ca. 5 mm below the mixed-phase port with extract solvent, sufficient to immerse the agitators completely. Agitation was started and the feed rates of the solvents were adjusted to the following values: raffinate phase to stage 1 (L), 15 $cm^3 min^{-1}$; extract phase to stage 12 (V), 45 $cm^3 min^{-1}$;

TABLE I

Characteristics of the Wool Greases

| | | Grease A | Grease B | Grease C |
|---|---|---|---|---|
| Saponification value (mg KOH/g) | | 81.3 | 107 | 95.4 |
| Acid value (mg KOH/g) | | 0.8 | 5.8 | 6.2 |
| Ash (%) | | 0.05 | 0.15 | 0.06 |
| Color: (Lovibond units) | Red | 0.5 | 2.2 | 3.1 |
| | Yellow | 1.0 | 17 | 36 |
| | Blue | 0.1 | 0 | 0.7 |
| Detergent (% w/w) | | | | |
| | N2 | 0.01 | 0.00 | 0.02 |
| | N3 | 0.05 | 0.03 | nd |
| | N4 | 0.11 | 0.08 | 0.37 |
| | N5 | 0.15 | 0.13 | 0.39 |
| | N6 | 0.24 | 0.25 | 0.54 |
| | N7 | 0.28 | 0.29 | 0.55 |
| | N8 | 0.29 | 0.28 | 0.45 |
| | N9 | 0.27 | 0.27 | 0.39 |
| | N10 | 0.21 | 0.21 | 0.24 |
| | N11 | 0.17 | 0.17 | 0.14 |
| | ≥N12 | 0.18 | 0.18 | 0.14 |
| Free cholesterol (% w/w) | | 2.4 | 4.3 | 4.9 |

nd = not determined.

and wool-grease feed solution to stage 5 ($L_F$), 25 $cm^3 min^{-1}$. The extract-phase discharge was adjusted as necessary by valve V4 to maintain the interfacial level below the mixed-phase port.

The instantaneous flow rates of solvents into and out of the apparatus were monitored by the rotameters (R1, R2, R3 and R4). However, flow rates for use in mass-balance calculations (Table II) were calculated from the measured volume of solvent either fed to or discharged from the mixer-settler during the operating period.

After 12 hr operation when the mixer-settler had reached steady state (10), aliquots of the hexane-rich phase (10.00 mL) and the IPA-rich phase (30.00 mL) were withdrawn from each settling compartment and evaporated to dryness (residues A).

At the end of each run, the product extract and raffinate phases were evaporated in a climbing film evaporator operating under vacuum. The residues (B) of each phase were weighed.

**TABLE II**

Operating Conditions for the 3 Extractions

| Solvent stream | Flow rate | | |
| --- | --- | --- | --- |
| | Grease A (cm$^3$ min$^{-1}$) | Grease B (cm$^3$ min$^{-1}$) | Grease C (cm$^3$ min$^{-1}$) |
| Raffinate to stage 1 (L) | 13.8 | 18.3 | 14.7 |
| Hexane feed to stage 5 (L$_F$) | 24.1 | 23.8 | 24.1 |
| Extract to stage 12 (V) | 47.5 | 39.2 | 41.2 |
| Solvent ratios | Grease A | Grease B | Grease C |
| Enriching ratio $\dfrac{(L)}{(L_F)}$ | 0.57 | 0.77 | 0.61 |
| Extraction ratio $\dfrac{(V)}{(L_F)}$ | 1.97 | 1.65 | 1.71 |

## Analytical

Samples of the initial greases (0.100 g), residues A (total material) and residues B (0.100 g) were redissolved in 10.00 mL of dichloromethane/heptane (1:1, v/v). All sample solutions were analyzed for free cholesterol and nonyl-phenol ethoxylate detergent by high performance liquid chromatography (HPLC) methods described elsewhere (8).

Acid value, saponification value and ash content were determined by standard methods (13). Color was measured in a Lovibond tintometer with a $^1/_8$-in. cell (5).

## Bleaching

Samples of wool grease (100 g) were bleached according to the procedure of Anderson and Wood (14).

## RESULTS AND DISCUSSION

### Solvent Flow Rates

Solvent flow rates for the extractions of the three wool greases (Table II) were selected with the aid of the design procedure (9) so that the ratios (V/L$_F$ and L/L$_F$) would enable all detergent oligomers with more than 7 ethoxylate units to be removed from the wool grease, with the loss of esters kept sufficiently small to ensure economic viability.

Ideally, the raffinate and extract phases should have been immiscible. Consequently, solvent flow rates should have remained constant from stage to stage, except at stage 5 where additional raffinate solvent was added. For the high-quality wool grease (grease A), performance approached the ideal and measured output flow rates of both raffinate and extract were in close agreement with their respective total inputs. For greases B and C, solvent immiscibility was also satisfactory; however, behavior departed from the ideal in another respect. The separation of the solvent phases in settling compartment 1 was incomplete, causing entrainment of hexane-rich solvent in the final extract (for grease B, 4% v/v; for grease C, 20% v/v). A factor that contributed to the slow phase separation in settler 1 was the relatively high concentration of surface-active components, such as detergent, in the final extract. In future applications the problem could be overcome by increasing the residence time in the settling compartments of stages 1-4 in the enriching section. (For greases B and C, the residence time of the extract phase was ca. 3.4 min.)

### Characteristics of the Product Wool-Grease Fractions

The characteristics of the wool-grease fractions recovered from the raffinate and extract phases of the three extrac-

tion runs are given in Table III. For the two lower quality greases (B and C), the hexane-rich solvent entrained in the final extract phase was decanted and evaporated separately to yield an additional wool-grease fraction. The sum of the raffinate and extract mass fractions is not necessarily 100%, because of grease losses when the apparatus was drained at the end of the run.

No detergent oligomers containing 7 or more ethoxylate units in their hydrophilic chain (N7, N8, N9 ... ) were detected in the raffinate product of any experiment. Apart from grease C, no significant concentrations of components with shorter hydrophilic chains (N6, N5, N4 ...) were detected in the raffinate products.

The presence of short-chain oligomers in the raffinate product of grease C resulted from a combination of the following: (a) the reduction in the distribution coefficient of detergent oligomers in favor of the IPA-rich phase as the ethoxylate chain shortened (10); and (b) the high concentration of the short-chain oligomers in the crude Lo-flo grease.

If the distribution of ethoxylate chainlengths for the detergent present in grease C is compared with that for the detergent added to the scouring liquors (Fig. 3), it may be seen that the oligomers with short ethoxylate chains (N2-N6) were preferentially recovered in the grease phase under Lo-flo scouring conditions. N3 was not determined in grease C because of the poor resolution of the N3 peaks in the HPLC chromatogram.

Mass flow rates of selected detergent oligomers leaving the individual extraction stages in the extract and raffinate phases for the extraction of grease C were calculated from the concentrations of the components in the samples collected after 12 hr operation and the average solvent flow rates (Table II). The results (Fig. 4) show that components with 7 or more ethoxylate units in the hydrophilic chain were rapidly removed by the aqueous IPA and were not detected in the raffinate leaving stages 7-12.

Short-chain oligomers (N6, N5, N4 ...) took progressively more stages to be removed from the raffinate. To achieve a greater removal of the short oligomers would require that either the number of stages in the stripping section or the extraction ratio, V/L$_F$, be increased.

The results (Table III) show that the separations of components achieved by dual-solvent extraction are in close agreement with those forecast by the multicomponent model developed earlier (9). Thus, for moderate flow rates of solvent relative to the feed (L/L$_F$ = 0.5; V/L$_F$ = 1.5), esters and free cholesterol remain almost entirely in the raffinate phase; part of the free acids are removed by the extract; and for typical commercial greases (A and B),

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**TABLE III**

Characteristics of the Wool-Grease Fractions

| | | Grease A | | Grease B | | | Grease C | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Raffinate | Extract | Raffinate | Extract | | Raffinate | Extract | |
| | | | | | hexane-rich | IPA-rich | | hexane-rich | IPA-rich |
| Mass fraction of the grease input (%) | | 87.2 | 7.5 | 91.1 | 3.7 | 5.4 | 82.6 | 6.3 | 4.8 |
| Saponification value | | 78.5 | 64.5 | 104 | 95.4 | 92.6 | 87.0 | 90.0 | 59.0 |
| Acid value | | 0.6 | 1.1 | 4.4 | 4.2 | 12.8 | 5.6 | 6.1 | 8.3 |
| Ash (%) | | 0.01 | 0.29 | 0.08 | 0.18 | 1.5 | 0.05 | 0.07 | 0.11 |
| Color: | red | 0.2 | 3.2 | 1.6 | 2.4 | 14.9 | 1.9 | 2.2 | 8.6 |
| (Lovibond | yellow | 1.0 | 2.1 | 12 | 18 | 62 | 13 | 0.7 | 79 |
| units) | blue | 0.1 | 2.3 | 0 | 0.2 | 6.8 | 0 | 0 | 0.7 |
| Detergent (% w/w) | N2 | 0.00 | nd | 0.00 | 0.01 | 0.06 | 0.01 | 0.1 | 0.1 |
| | N3 | 0.00 | 0.38 | 0.01 | 0.05 | 0.22 | nd | nd | 1.2 |
| | N4 | 0.00 | 0.99 | 0.00 | 0.16 | 1.18 | 0.17 | 0.5 | 2.3 |
| | N5 | 0.00 | 1.39 | 0.00 | 0.17 | 2.28 | 0.14 | 0.6 | 4.3 |
| | N6 | 0.00 | 2.67 | 0.00 | 0.33 | 5.09 | 0.11 | 0.6 | 7.9 |
| | N7 | 0.00 | 3.05 | 0.00 | 0.28 | 5.95 | 0.00 | 0.5 | 9.1 |
| | N8 | 0.00 | 2.93 | 0.00 | 0.00 | 6.15 | 0.00 | 0.3 | 8.6 |
| | N9 | 0.00 | 2.54 | 0.00 | 0.00 | nd | 0.00 | 0.0 | 7.2 |
| | N10 | 0.00 | 1.78 | 0.00 | 0.00 | nd | 0.00 | 0.0 | 4.7 |
| | N11 | 0.00 | nd | 0.00 | 0.00 | nd | 0.00 | 0.0 | 3.1 |
| | ≥N12 | 0.00 | nd | 0.00 | 0.00 | nd | 0.00 | 0.0 | 1.2 |
| Free cholesterol (% w/w) | | 2.4 | nd | 3.9 | 2.6 | 4.8 | 4.9 | 6.7 | 5.3 |

nd = not determined.
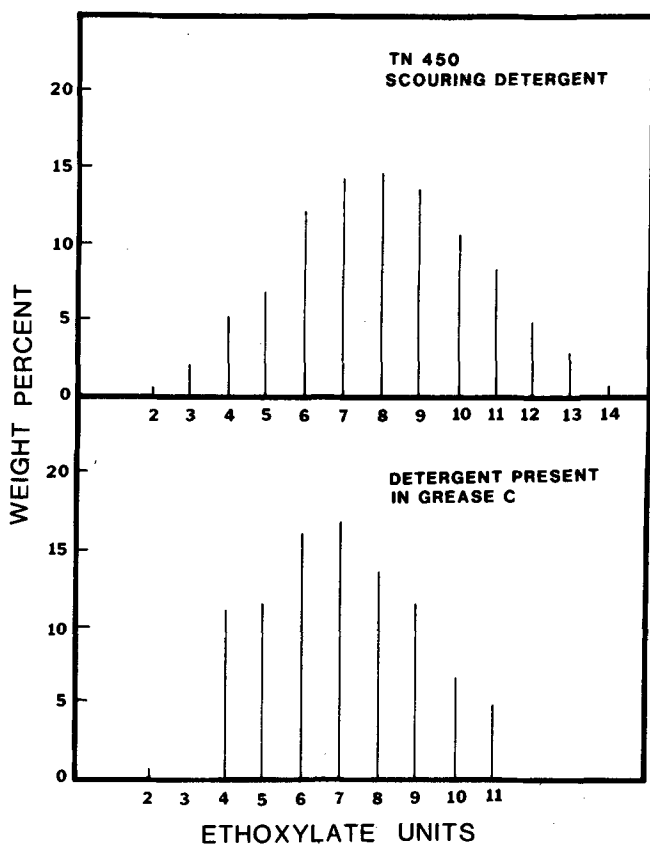


FIG. 3. Comparison of the ethoxylate chain length distributions of TN450 and the detergent present in grease C (Lo-flo crude grease).
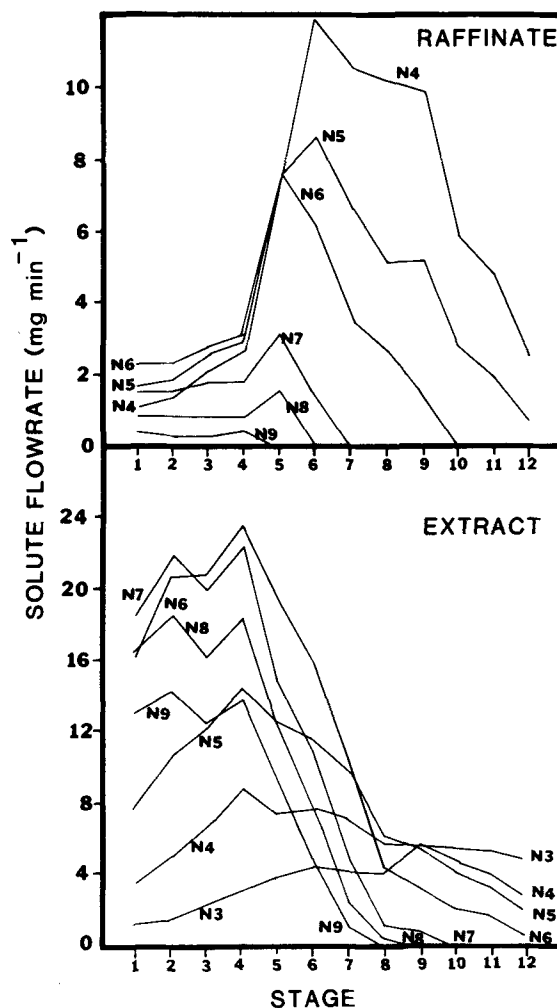


FIG. 4. Flow rate of detergent oligomers leaving stage 1 for grease C.

detergent is effectively removed by the extract.

The results also indicate that dual-solvent extraction has potential for refining wool grease on a commercial scale.

### The Effect of Prior Solvent Extraction on Bleaching

The color and bleachability of wool grease are important parameters, which help determine its commercial value. It was hoped that the oxidized components responsible for color (15) would be removed by dual-solvent extraction, but the improvement in grease color was only marginal (Table III). For the high-quality wool grease A the improvement, although small, resulted in a wool grease of excellent color.

The colors of greases B and C and their raffinate products before and after various bleaching treatments are given in Table IV.

**TABLE IV**

**The Color of Bleached and Unbleached Fractions**

| Sample | Treatment | | Color (Lovibond units) | | |
|---|---|---|---|---|---|
| | Acid added[a] (mL) | Peroxide added[b] (mL) | Red | Yellow | Blue |
| Grease B | | | | | |
| Crude | 0 | 0 | 2.2 | 17 | 0 |
| Crude | 1 | 4 | 0.8 | 6 | 0 |
| Raffinate | 0 | 0 | 1.6 | 12 | 0 |
| Raffinate | 1 | 2 | 0.8 | 9 | 0 |
| Raffinate | 1 | 4 | 0.8 | 5 | 0 |
| Raffinate | 0 | 2 | 1.9 | 16 | 0 |
| Raffinate | 0 | 4 | 1.7 | 16 | 0 |
| Grease C | | | | | |
| Crude | 0 | 0 | 3.1 | 36 | 0.7 |
| Crude | 1 | 4 | 1.2 | 5 | 0 |
| Raffinate | 0 | 0 | 1.9 | 13 | 0 |
| Raffinate | 1 | 2 | 1.2 | 10 | 0 |
| Raffinate | 1 | 4 | 1.0 | 8 | 0 |
| Raffinate | 0 | 2 | 1.2 | 9 | 0 |
| Raffinate | 0 | 4 | 1.1 | 8 | 0 |

[a]5% v/v sulfuric acid added to 100 g grease.
[b]30% v/v hydrogen peroxide added to 100 g grease.

As expected, treatment with 1% w/w of sulfuric acid (5% v/v) and 4% w/w of hydrogen peroxide (30% v/v) significantly improved the colors of crude greases B and C. However, the pretreatment of the two greases by solvent extraction had no significant effect on the color achieved by the bleaching process. The colored components removed by solvent extraction appear to have been those which were relatively easy to bleach.

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