Prepilot Plant Method for Crystallizing Fats and Greases in Drums[1]

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IN the evolution of a process from the laboratory to an integrated pilot plant it is frequently desirable to employ an intermediate or prepilot plant stage. In such a stage a new product can be produced in bulk for evaluation, and experience can be acquired in handling it. Information not conveniently obtained on a laboratory scale can be gained at this stage; for example, data on rates of filtration or settling and on bulk densities. A prepilot plant unit can frequently be improvised from existing equipment and operated advantageously while the specifically designed, integrated pilot plant is under construction.

This paper describes an improvised prepilot plant for the preparation of relatively large quantities of fats, greases, and their derivatives. Since little has been published on methods for preparing intermediate quantities of these materials, the primary purpose of this paper is to present such a method. It is also intended to give information on the solvent fractionation of unsaponified wool grease.

Wool grease, or crude lanolin as it is sometimes called, is a product obtained by scouring wool. The fraction was required to have prescribed viscosity characteristics and was to be prepared by fractional crystallization at reduced temperature from a solvent solution. About 400 pounds of product were required. To produce this amount entailed the handling of about 800 pounds of raw wool grease and 3,200 pounds of solvent. A thorough investigation would necessitate the installation of a continuous crystallization system for the study of cooling rates, crystallization temperatures, holding times, heat balances, and the like. The lack of equipment and the urgency of producing this relatively large quantity for immediate evaluation however did not permit such an elaborate study at the time.

Four operations were required: solution of the heated wool grease in a heated solvent; fractional crystallization of the wool grease from the solvent by cooling; filtration of the slurry thus formed; and stripping the solvent from each of the fractions obtained in the filtration.

A small refrigerated kettle was used in preparing the first few batches because in it cooling rates could be controlled. This system was not adaptable to production however because of its limited capacity, and it was discontinued after sufficient batches had been made to set up viscosity standards.

For the blending operation a vessel was needed which fulfilled the requirements of capacity, ease of cleaning, and means of agitation. It was essential also that the contents could be transferred readily to a cooling device or could be cooled in the vessel itself.

The 55-gallon drum met the requirements of capacity and ease of cleaning. In addition, the drum could be transferred to a refrigerated room maintained at a temperature below the required final crystallization temperature.

In preparing the wool grease-solvent solution, the solvent was displaced from its original 55-gallon drum by inert gas at low pressure through a cartridge filter and a 5-square-foot heat exchanger to a blending drum set on a drum-rolling device. The desired solvent temperature, as indicated by a thermometer at the heat-exchanger outlet, was maintained by adjusting the steam pressure on the heat-exchanger jacket and controlling the flow rate. Solvent rates as high as 1,200 pounds per hour were attained with gas pressures of about 2 or 3 p.s.i.g.; this pressure was below the 5 p.s.i.g. considered to be the top safe limit for the drums. For safety during the transfer of solvent the blending drum was vented to a point outside the building, and all containers and lines were grounded.

The wool grease was heated in its original 55-gallon, open-headed drum by inserting a "U" shaped heater of 1-inch pipe carrying low-pressure steam. When the required amount of solvent had been transferred at the desired temperature to the blending drum, transfer lines were removed, and the proper amount of wool grease added through a funnel. The blending drum was then rolled and cooled in room temperature air until the temperature of the solution reached about 105°F. It was then removed from the drum roller and transferred to a refrigerated room. When the final crystallization temperature was reached, as dictated by the viscosity ratio required in the final product (Figure 4), the blending drum was removed from the room, and the cold slurry was filtered on a rotary-drum vacuum filter of conventional design. The filter cake was weighed and samples were sent to the laboratory for analysis. The filtrate was weighed and the solvent was removed from it in a pot still.

In the blending operation 99% isopropanol and crude wool grease were mixed in the weight ratio of 3.9 to 1. The alcohol was heated to 140°F., and the wool grease was added at a temperature as near 140° F. as possible to determine qualitatively any heat effects. In each case an immediate cooling of the mixture was observed, indicating a heat of solution of about 3 BTU per pound of mixture. From the same data the specific heat of the wool grease was calculated to be approximately 0.7 BTU per pound per °F. Wool grease at 130° to 140°F. was fluid and easily pumped.

The blend was cooled and crystallized in a refrigerated room where the air temperature was maintained at 34 to 36°F. The drum was allowed to stand in this room, in still air, until the prescribed final temperature of the contents was reached. Agitation during crystallization of this material was found to be unnecessary. An electronic potentiometer continuously recorded the temperature of the contents of the drum as well as that of the surrounding air. From these

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[1] Report of a study made under the Research and Marketing Act of 1946.

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records time-temperature curves were drawn for each run; these were examined for temperature plateaus which would indicate heavy crystallization. Figure 1 shows a typical curve for wool grease. The absence of any plateau indicates that crystallization occurred continuously, pointing to a heterogeneity of the solid phase. Upon removal from the refrigerated room, the drum was rolled for about 5 minutes on the drum-rolling machine. This time was found to be ample for loosening any crystals adhering to the inner surfaces of the drum and to produce a uniform slurry for filtration.

The slurry was fed directly from the drum to the trough of a rotary-drum vacuum filter continuously by means of a variable-speed, positive-delivery pump. The transfer lines and filter trough were insulated to prevent excessive heat pickup by the slurry. Temperatures of feed and filtrate were recorded for quality control. Rates of filtrate and cake discharge were noted to determine the extent of diminution of filtration rate with time. Figure 2 represents a time-rate curve for wool grease slurries filtered on a 3-square-foot filter through 6-ounce canvas cloth. With this particular cloth the rate dropped off sharply. Washing the cloth in place however restored it to its original efficiency. Neither the cake nor the cloth was washed during the runs, but the cloth was washed thoroughly between runs. Filter cakes were produced containing from 53 to 59 weight % solids and were easily removed by blowing a small amount of low-pressure air through the cloth. This operation is shown in Figure 3.

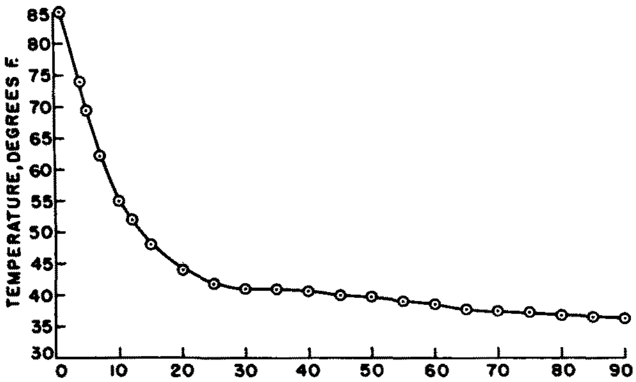

FIG. 1. Typical cooling curve for wool grease solutions.

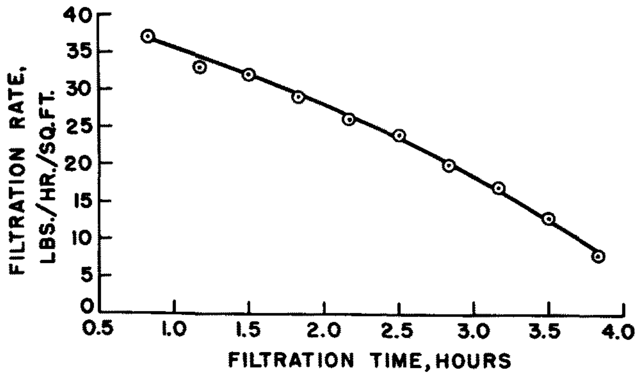

FIG. 2. Filtration rate vs. filtration time for wool grease slurries.

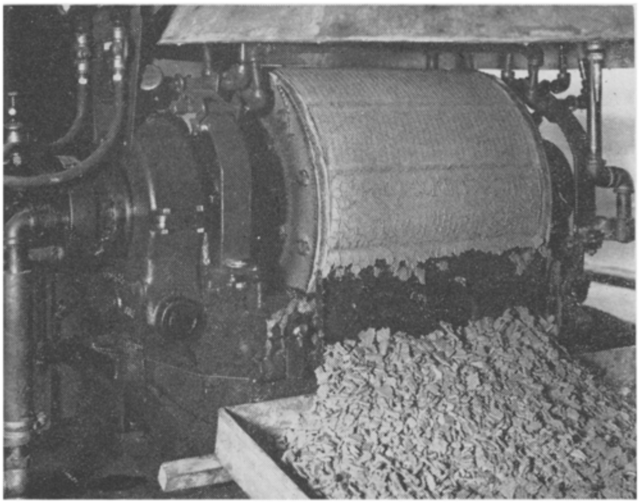

FIG. 3. Filter drum discharging wool grease solids.

Solvent was removed from the solid and liquid fractions batchwise by evaporation in a glass-lined still, mainly at atmospheric pressure but with final stripping at reduced pressure.

Liquid fractions amounting to 60-65% of the original wool grease were recovered in the stripping operations. Viscosities of the fractions in carbon tetrachloride solution were determined at 41° and 86°F. (5° and 30°C.). These fractions were to be used as a base in sheep-branding paints in the blending of which carbon tetrachloride was used as a thinner. For this reason the same solvent was employed in the same ratio (40.3 weight % CCl_4, 59.7 weight % wool grease) for viscosity determinations. Liquid fractions were evaluated on the basis of their viscosity ratio, that is, viscosity at 41° divided by viscosity at 86°F. It was found that this ratio could be reduced from the value of 35 for whole wool grease to approximately 5 for liquid fractions obtained by crystallizing at 41°F.(5°C.), and such fractions were found to be satisfactory for applying as paints because of their low rates of viscosity change with temperature. Figure 4 shows the effect of crystallization temperature on viscosity ratio.

These data indicate that fractions of any desired ratio below 35 can be prepared by the proper choice of crystallization temperature.

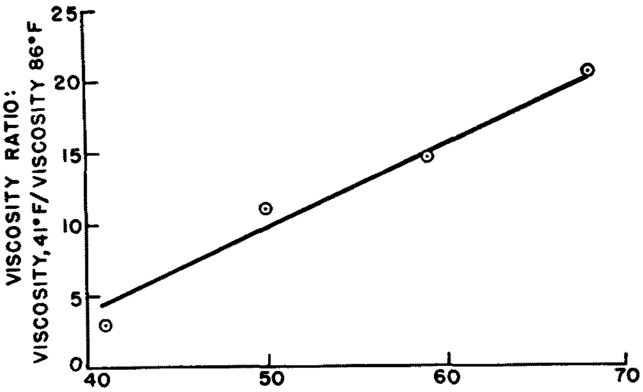

FIG. 4. Effect of crystallization temperature on viscosity ratio of wool grease filtrates.

This same general method has been used to good advantage in the preparation of quantities of high purity stearic and palmitic acids. In the case of stearic acid the raw material containing 80% stearic and 20% palmitic acids by weight was melted and dissolved in isopropanol in the weight ratio of 1 part of acids to 8.3 to 9.4 parts of alcohol at about 130°F. This solution was cooled to 50°F. and filtered in the same manner as the wool grease, except that the cake was washed continuously on the filter drum with cold alcohol. Stearic acid product of 92 to 96.5 weight % purity was prepared by this method. In the preparation of palmitic acid, acetone was used as the solvent, and the raw material was dissolved in the weight ratio of 1 part of acids to 12 parts of acetone at 100° F., cooled at 35° F., filtered, washed, and stripped of solvent. Palmitic acid having purity greater than 90% was produced.

Experience in preparing the three products described has shown that the method of fractional crystallization employing the 55-gallon drum is of value in making large samples of certain new products for evaluation prior to installation of integrated pilot-plant facilities. Also the information gained in handling the raw materials and final products in the improvised equipment has been of considerable aid in pointing out a more practical approach to the design of final pilot-plant equipment.

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Spectrochemical Determination of Iron and Copper in Commercial Oils[1]

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ESTABLISHMENT of the relationship between copper and iron content and flavor stability of salad oils required an analytical method for these elements with a sensitivity of approximately 0.01 p.p.m. This sensitivity was estimated from flavor changes caused by additions of small quantities of copper and iron compounds to an oil which had exceptional flavor and storage qualities. Since the amount of sample available for metal analysis often was limited, a method was desired from which duplicate results for both copper and iron could be obtained on 100 grams of oil or less. The spectrochemical method was selected because of its sensitivity and specificity. Analyses have shown that some oils contain less than 0.01 p.p.m. copper whereas the iron content of all oils analyzed has exceeded this concentration.

Attempts were made to analyze the oil directly in the arc, a method which is used for additives in lubricants (1), but it was found that this method did not have sufficient sensitivity.

O'Connor (5) has published a spectrochemical method for determining as low as 0.1 p.p.m. copper and iron in oils. We have modified his ashing technique so that duplicate results for both copper and iron may be determined on a 40-gram oil sample containing as little as 0.001 p.p.m. copper and 0.01 p.p.m. iron.

Wet ashing methods, which are widely used on organic materials, were found to be unsatisfactory in this instance because of the large amounts of mineral acids necessary, the size of container required to carry out the decomposition, and the difficulty of reducing the volume of the resulting solution.

It is well known that elements other than those being determined may influence the intensity of the spectral lines of the elements of interest. For this reason a semi-quantitative analysis of 16 different commercial oils from seven companies was carried out to determine the major metallic constituents. The ash was found to be composed of calcium, magnesium, and sodium compounds in varying relative amounts. Each of these was found to enhance the intensities of the iron lines several-fold and the copper lines to a lesser extent.

The ash content of two commercially refined oils was determined and found to be approximately 30 p.p.m.; by contrast the ash content of seven laboratory-refined oils was found to be 10 p.p.m. or less (6). In order to overcome the variability caused by the approximately 0.5 mg. ash obtained from 20 grams of commercially refined oil, calcium, magnesium, and sodium nitrates were added to each oil sample before ashing. These salts were chosen for their solubility in organic solvents, as well as for their decomposition in the presence of organic material, to form a matrix consisting of carbonates and oxides. This addition increased each of the major metallic constituents to such a level that the small variation caused by the ash no longer has an effect on line intensity. The matrix also acts as a carrier for the extremely small amount of ash obtained from many refined oils. In the case of many laboratory-refined oils it was impossible to see the ash resulting from 20 grams of oil.

Preparation of Ash and Standards

Oil samples of 20 grams or less were weighed into 100-ml. Pyrex beakers. In the case of crude oils the sample weight required has been as low as 0.50 gram. An internal standard, consisting of 5.88×10^{-3} mg. beryllium nitrate in methyl ethyl ketone together with 4.9 mg. calcium nitrate, 3.7 mg. magnesium nitrate, and 1.6 mg. sodium nitrate dissolved in methyl alcohol, was added to each sample before ashing. The samples were then partially decomposed by slow pyrolysis on a hot plate. The initial hot plate temperature was approximately 350° C. and was increased stepwise to 450°C. Pyrolysis was carried out at a rate sufficiently slow to avoid mechanical loss of sample by spraying and violent bubbling. Treated in this manner, the samples seldom burst into flame; however analyses have shown no appreciable loss of copper or iron in those samples which did ignite. Decomposition on the hot plate required approximately 18 hours. The charred samples were then transferred to a muffle furnace and ashed at 450°C. The ashing

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