

(molar basis). That the data in Table II do not correspond quite closely with such S_3 figures is largely a result of variation in natural lards. It is evident from Table II that, in those S_3 -free test samples, slight hydrogenation itself or interesterification itself does not destroy the β' -3-tendency of lard, but combined hydrogenation and interesterification do. Hydrogenation presumably plays a role, though a small one, in reducing β' -3-tendency of modified lard, hence probably in reducing graininess potential.

The greater β' -2 tendency of the interesterified lards of Table I than that in Table II is believed to be due to the S_3 content in those of Table I, rather than to difference in crystallizing conditions.

Broadly speaking, the elimination of graininess in lard shortening results from a change in the disaturated glycerides which comprise $\frac{1}{4}$ of the lard, natural or interesterified. The β' -3-tending disaturated OPS is exchanged for a mixture of disaturated glycerides, lower melting, i.e. more soluble, and tending to crystallize in the more familiar β' -2 form which is the typical form of hydrogenated vegetable oil shortenings.

Directed interesterification of lard (3,4,5,8,9) results in production of S_3 or hardstock *in situ* and a consequent reduction in the "random mixture" of β' -2-tending disaturated glycerides. There results both an improvement in plastic range and reduced graininess potential.

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Studies in Soap Crystallization Processes. Part III. Acid Soap Crystallization in the Segregation of Tall Oil Fatty Acids

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Abstract

Tall oil fatty acids have been fractionated into 80–90% oleic acid, and 60–80% linoleic acid fractions, by precipitation of the oleic acid as acid soap from polar solvents. Sodium and potassium acid soaps are equally effective, but ammonium acid soaps require lower operating temperatures. The choice of solvent is not critical as regards degree of separation, but technically attractive filtration rates have been obtained only with methanol and acetone. Acidulation gives colorless oleic acid of very low rosin acid and unsaponifiable content, but with 5–10% of conjugated linoleic acid.

TALL OIL is a mixture of approximately equal parts of rosin acids and fatty acids, the latter being themselves a 50:50 mixture of oleic and linoleic acids. The "oil" is in steady supply as a by-product of the kraft paper industry, and there is ample fractionating capacity for separation into rosin and fatty acids. If the fatty acids could be further separated into high linoleic and high oleic fractions, then there would be available new tonnage sources of high drying value acids for the alkyd industry, and of oleic acid, independent of its usual tallow source, and with a nonfluctuating supply background suitable for its proper consideration as a heavy organic chemical intermediate. Tall oil fatty acids are accordingly an attractive substrate for the investigation of oleic/linoleic separations.

Oleic and linoleic acids have been separated completely by elution chromatography, using hexane and silicic acid; by gas phase chromatography, using polyester stationary phases; and by countercurrent distribution, using hexane and acetonitrile in a Craig machine. A high degree of separation has been achieved

by vacuum fractionation, using high reflux ratios in high efficiency columns, and lesser degrees by crystallization from solvents, by urea complexing, and by thermal diffusion. Preceding most of these methods, Freeman's (1) separation by countercurrent distribution between furfural and hexane was carried through to a large pilot plant scale by Gloyer in 1948 (2).

Difficulties in the above methods are various: chromatographic methods have yet to emerge from the laboratory scale; vacuum distillation demands an uneconomical reflux ratio and column design; cold crystallization is complicated by the very wet low temperature filter cakes, 20% solids appearing "dry" at -30°C ; and thermal diffusion calls for a heat flux of some 100,000 BTU per lb of product treated. The Gloyer method is straightforward, and is the only one so far to merit the term "process."

Crystallization of soaps has been of little value so far in this field; the lithium soap method for oleic acid is the only reasonably successful application, but work in progress on the crystallization of soaps of substituted fatty acids indicated that acid soaps were capable of giving useful degrees of separation in rather unexpected cases; promising results were obtained as soon as the method was applied to tall oil fatty acids. The acid soaps referred to are well authenticated substances in the saturated fatty acid field having the composition $\text{R-COOH.R-COO}(\text{Na, K, or NH}_4)$; they are appreciably less soluble in alcohols than the corresponding neutral soaps, and have the added advantage of a good crystal habit. In the unsaturated fatty acids, however, only a single acid soap has been described, potassium hydrogen dioleate having been prepared by McBain and Stewart as far back as 1927 (3). Ralston (4), without source reference, gives solubilities of 4.3% (1.34M) for neutral potassium oleate, and 6.5% (1.30M) for the acid soap, fig-

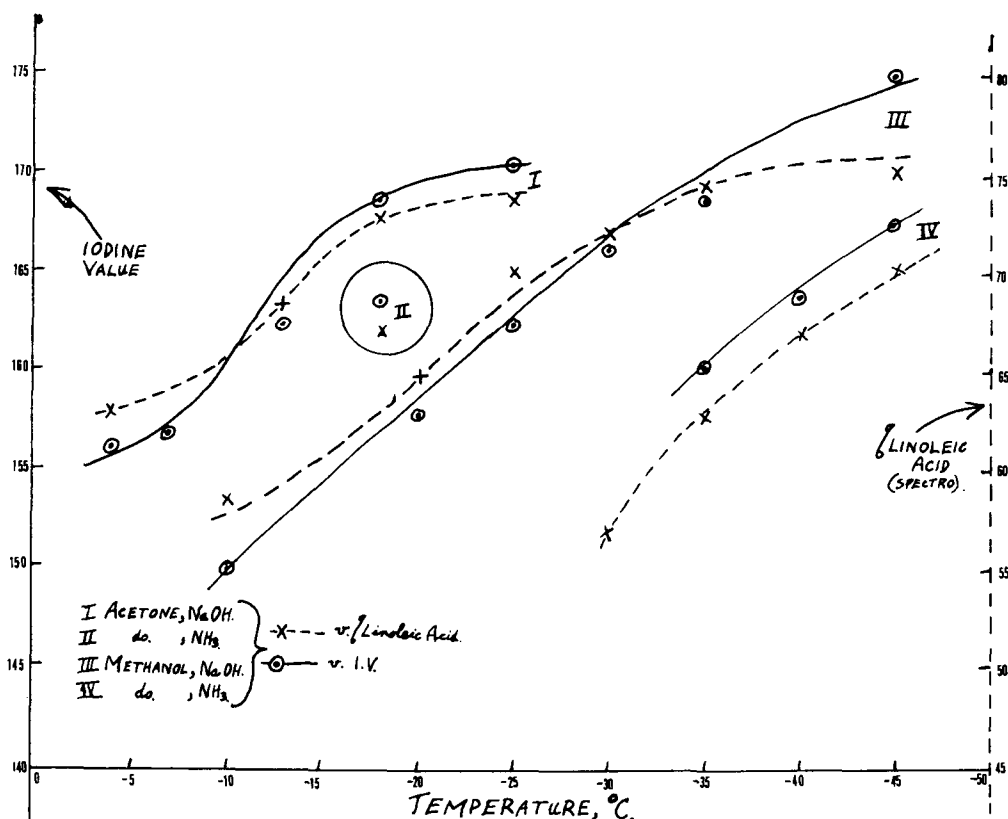


FIG. 1. Fractionation of tall oil fatty acids: the effects of temperature on I.V. and per cent linoleic acid of the soluble fraction.

ures which indicate a somewhat marginal existence for unsaturated acid soaps, and evidence of these soaps being only metastable was obtained in the present work.

Experimental

Tall oil fatty acids were half neutralized with NaOH in methanol and heated in vacuum to 100C to produce an almost anhydrous solution of soap in the excess fatty acid. This was then added to 4 vol of solvent, giving solutions which were cooled to around -20C. It was immediately apparent that nonpolar solvents failed, giving gelatinous systems, but that polar solvents gave crystalline precipitates, the solvents of lowest molecular weight giving the best formed crystals and the best filtrations.

Methyl acetate, ethyl acetate, acetonitrile, acetone, methyl ethyl ketone, methanol, ethanol, isopropanol, and butanol all gave similar enrichments in the soluble linoleic acid fraction, but only methanol, acetone, and the esters gave crystals which were easy to filter and wash. Filtration difficulties with the less successful solvents led to slow washing and some redissolution of the solid phase, causing lower yields of the oleic fraction, together with intermediate wash liquor fractions. Acetone and methanol were outstanding with respect to speeds of filtration and washing, and therefore were selected for the bulk of the work.

The degree of neutralization can be varied over a wide range, from only enough to half-neutralize the oleic acid, up to enough for at least 60% neutralization of all fatty acids present, with the acid soap remaining the stable solid phase under operating conditions. To some extent a higher degree of neutralization can be exchanged for reduced refrigeration. Thus with acetone at 0C, 20% neutralization gives a 35% yield of oleic acid of I.V. below 90, and linoleic acid of I.V. around 150. As the neutralization rises towards 50%, the I.V. of the oleic acid rises to 110,

and the linoleic acid to 160, but its yield drops to below 40%. Also 30% neutralization and +5C gave very similar results to the above ones for 20% and 0C.

The effect of temperature is in the expected direction; lowering the temperature at a constant degree of neutralization leads to a more complete precipitation of the oleic acid, together with an increase in its linoleic acid content. A change from acetone to methanol needs a 10C drop in temperature to achieve the same degree of separation, and a further change from alkali metal to ammonia neutralization calls for a further drop of 20C to maintain the result. A single check on ammonium vs. sodium in acetone indicated a lesser temperature dependence of about one-half of this figure (Fig. 1).

Either sodium, potassium, or ammonium acid soaps can be used for the precipitation, and there is little difference between the two alkali metals. Ammonia requires lower operating temperatures to get the same results. Theoretically ammonium soaps can be completely dissociated by heat, steam, and vacuum, allowing the ammonia to be recovered directly; but in practice it is difficult to avoid slight amide formation, and considerable formation of color bodies. This is a serious disadvantage, as careful acidulation of the alkali metal acid soaps gives a water white oleic acid without distillation. The need to keep ammonia out of recycle acetone is a further limitation.

The volume of solvent required is similar to that used for conventional fatty acid crystallization, being about three volumes for the precipitation and another one or two volumes for washing, though both of these quantities can be reduced for any recrystallization of the acid oleate. Lower solvent usage gives smaller crystals and poor filtration, and higher volumes require lower temperatures for the same yield, though this combination gives a small increase in selectivity, leading to a purer oleic acid. Methanol gives a slower

crystallization than acetone, larger crystals and better filtration rates, and so allows also the lower range of wash liquor usage. Completely anhydrous conditions generally give poor crystallization, and from 2 to 5% of water in the system is desirable. Larger amounts of water can be used with higher degrees of neutralization, especially in recrystallizations, where maximum recovery is required, and the degree of neutralization is already 50%.

The working up of the linoleic acid fraction from the filtrate is simple because of its low soap content under optimum conditions. The solvent can be distilled off without foaming, even in the presence of stripping steam; and the slightly neutralized fatty acids left can be fully split in the usual manner. If this fraction is to be vacuum distilled, the residual alkali can be left unneutralized, as little trouble was experienced in distilling low soap content acids. The bottoms (if removed at 50% FFA) have been found to remain fluid down to ambient temperature, behavior rather different from that found with lower I.V. materials.

The filter cake of acid oleate is more difficult to handle. When methanol has been the solvent, the avoidance of esterification calls for complete solvent removal before acidification, but this is not necessary when acetone has been used. In either case, the solvent boils at a relatively low temperature, at which the molten acid soap is extremely viscous and liable to froth badly. This can be avoided by charging the filter cake directly into a vessel maintained at above 120C so that the solvent and any water are flashed off. The greatly lowered viscosities found at this temperature allow of only slight foaming. At 140C stripping steam can again be used without trouble. Alternatively, part of the acidulated acid soap can be recycled, and then the acid soaps dissolve to give low viscosity nonfoaming solutions which can be stripped easily. As a batch process, particularly for laboratory preparations, acetone wet cakes can be dumped into hot acidulated water. Using vigorous stirring, particularly of the vibrating mixer type, large pieces of up to an inch cube are readily handled.

Typical Experiments

280 g of tall oil fatty acids were diluted with 840 ml 95% acetone, and 30 g 40% aqueous caustic soda added with good agitation, giving 30% neutralization, after which the solution was cooled slowly to -20C with occasional shaking. The crystalline slurry was filtered in a freezer chest at -20C and washed with acetone precooled to -20C until the washings were colorless. The filtrate and washings were evaporated down, and the solvent-free residue split with hot dilute acid, giving a linoleic acid concentrate of I.V. 169.0, linoleic acid (spectro) 78.6%. The filter cake was acidulated by dropping into well stirred 10% sulphuric acid at 80C, the oleic acid layer washed with hot distilled water, and dried in vacuum. The oleic acid was colorless; I.V. 99.5, A.V. 200.5, unsap. 0.1%. The yield was 54% of oleic and 46% of linoleic acid fractions.

280 g. of tall oil fatty acids were diluted with 840 ml 95% methanol, and 20 ml. of 10.0 N KOH added with stirring, giving 20% neutralization, after which the solution was cooled slowly to -5C with occasional stirring. Filtration at -5C, washing with methanol which had been precooled to -20C, and drying of the solid in a thin layer in an open room at an ambient temperature around 0C, followed. The solid and fil-

trate were then worked up as above, giving oleic acid (36% yield, I.V. 88) and linoleic acid (64% yield, I.V. 154.5, linoleic acid 64.1%).

Discussion

Limitations of the acid soap process are related to the nature of tall oil fatty acids, and probably also to the structure of the acid soaps. Acid soap crystallization involves pairing up of fatty acid molecules, as in soaps of divalent metals, and so an acid soap is like a lead soap separation rather than a fatty acid crystallization. Thus sodium hydrogen oleate-palmitate probably occurs at one extreme, and oleate-linoleate at the other, causing a lack of precision in both the saturated/unsaturated and the monoethenoid/diethenoid separations. Higher melting forms such as *trans* and "off centre" isomers also concentrate in the crystallized phase. Tall oil fatty acids are not exactly a 50:50 mixture of oleic and linoleic acids, as several per cent of saturated acids, and up to 15% of conjugated linoleic acid, are present; both of these segregate with the oleic acid, limiting its purity to some 80-90%. A high I.V. component, not returned as linoleic or linolenic acid by alkali conjugation, is also present: the linoleic acid fraction can achieve a peak I.V. of 175, using methanol at -45C, or 170 using acetone at -30C, but the linoleic acid contents determined spectrophotometrically are only about 80 and 75%. Even with the 0C acetone process, leading to an I.V. of 155, the linoleic acid assays only 65% against the expected 70%. The residual rosin acids, the color bodies, and unsaponifiable material also concentrate in the liquid fraction, leading to an increase of 50-100% in each of these respects, but allowing the oleic acid to be water white and almost free from both rosin acids and unsaponifiable matter.

The acid soaps of oleic acid are well crystallized compounds, but appear to be metastable with respect to a mixture of neutral soap and free acid. They melt incongruently over a wide temperature range giving viscous melts which do not resolidify on cooling and prolonged keeping, they are decomposed by non-polar solvents to give gels which lose oleic acid by syneresis, and they are unstable on storage unless solvent free and anhydrous. Potassium hydrogen dioleate has been stored without decomposition at room temperature for 3 years, but only in the case of recrystallized samples; sodium hydrogen dielaidate has also shown good stability. All samples analyzed have corresponded exactly to the 1:1 acid soap formulation.

Using the sodium acid soap/acetone process at 0C, with 25% mole per cent neutralization, some 40% yield of I.V. 90 oleic acid, and 60% of I.V. 155 linoleic acid may be obtained. Extrapolating this to the current availability of tall oil fatty acids, some 200 million lb of linoleic acid concentrate, and a challenging 150 million lb addition to the current oleic acid supply are potentially available.

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