2. Budowski, Pierre, and Markley, K. S., Chem. Rev., *48*, 125 (1951).
3. Morgareidge, Kenneth, Ind. Eng. Chem., Anal. Ed., *14*, 700 (1942).
4. Morton, R. A., and Stubbs, A. L., Analyst, *71*, 348 (1946); Biochem. J., *41*, 525 (1947); and *42*, 195 (1948).
5. Zscheile, F. P., and Henry, R. L., Ind. Eng. Chem., Anal. Ed., *14*, 422 (1942).

[Received March 3, 1953]

Solubility and Swelling of Metallic Ricinoleates in Solvents

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METALLIC ricinoleates belong to a class of materials known as metallic soaps, which in turn are commonly defined as the alkaline-earth and heavy metal salts of monobasic organic acids. Metallic soaps are characterized by a unique structure in that they combine in one molecule a *non-polar* organic radical with a *polar* carboxyl group having one hydrogen replaced by metal. It is the presence of these two dissimilar groups in a single molecule which accounts for the many interesting and commercially important applications for metallic soaps.

The metallic stearates (aluminum, zinc, calcium) and the metallic naphthenates (lead, cobalt, manganese, copper) are well known metallic soaps and account for about 70% of the annual United States metallic soap production of some 40,000,000 pounds (1949). Hundreds of other metallic soaps are theoretically possible, but relatively few have achieved the commercial importance of the metallic soaps noted above. In many cases this has been due a) to lack of knowledge concerning them and b) to the fact that they have not been commercially available.

Within the past year a group of soaps based on the fatty acids of castor oil, and known as the metallic ricinoleates, have been brought from relative obscurity to a stage where full scale production is now under way. Castor oil, itself, is differentiated from other fatty oils by the presence of a hydroxyl group on the 12th carbon atom of its principal fatty acid (ricinoleic acid). This feature leads to unusual properties, such as solubility of castor oil in alcohol, the only fatty oil to be so soluble. In turn it was conjectured that the presence of this hydroxyl group might also confer unique solubility properties to those metallic soaps derived from castor oil.

It is the purpose of this paper to report on five of these soaps and specifically on their solubility and swelling characteristics. It is felt that this information will be of distinct value in developing useful applications for these relatively new products.

Three of these metallic ricinoleate soaps (or salts), based on the fatty acids of castor oil, are being supplied to the trade as fine white powders. In appearance they are quite similar to their metallic stearate counterparts. A fourth metallic ricinoleate, magnesium ricinoleate, is supplied in the form of coarse white granules which tend to fuse together on standing. The fifth metallic ricinoleate, aluminum ricinoleate, is supplied as a taffy-like product. Metallic stearates corresponding to these five metallic ricinoleates are also included as reference materials in developing this solubility information.

The literature has little to say about the solubility of metallic ricinoleates. For example, Doss (1) in his recent excellent and comprehensive compendium of data on fatty acid salts was able to locate and report only the briefest information on metallic ricinoleate solubility as drawn from six references out of a total of 612 references on metallic soaps in general. Hence it was decided to determine in some detail the solubility characteristics of aluminum, barium, calcium, magnesium, and zinc ricinoleates. Only factual data is reported, and no attempt has been made to theorize or otherwise interpret the results obtained.

In planning the study on solubility, it was decided to work first with only two concentrations (25% and 50%) of the five metallic ricinoleates in selected solvents. From this screening evaluation more detailed study could be made as indicated. Parallel solubility tests were also run on the five corresponding metallic stearates to give a comparison reference system.

The 25% and 50% solution concentrations were made up as follows in some 25 solvents:

Procedure for Preparing 25% Concentration of Metallic Soap

a) 25 g. of soap were placed in a tared 250-ml. Erlenmeyer flask.
b) 75 g. of solvent were added.
c) The contents of the flask were refluxed on a steam bath for three hours.
d) The flask was then removed from the steam bath and immediately stirred to insure a uniform composition.
e) Before allowing the mix to cool to room temperature, a representative sample was poured into a 50 ml. test tube.
f) The filled test tube was stoppered and placed in a rack for observation after aging at room temperature for 24 hours and 30 days.

Procedure for Preparing 50% Concentration of Metallic Soap

a) 50 g. of soap were placed in a tared 250-ml. beaker.
b) 50 g. of solvent were added, and the mix was stirred to insure a uniformity of composition.
c) This mix was then passed through a three-roll laboratory paint mill three or four times to achieve a uniform dispersion of soap in the solvent
d) The dispersed product obtained by the milling procedure was returned to the 250-ml. beaker and the solvent loss sustained during milling determined.
e) Any required makeup of solvent was added, and the mix was given a final pass through the mill.
f) A 50-ml. test tube was filled with the final dispersion and stoppered.
g) The filled test tube was then placed in a rack and observed after aging at room temperature for 24 hours and 30 days.

A mechanical dispersion method was used for obtaining the 50% soap concentrations since it was believed some difficulty might be experienced in obtaining such concentrated solutions by heating. However subsequent work showed heating could be used although equivalent end results were not necessarily obtained.

The mechanical dispersion was not feasible for the 25% concentration since, in general, the mixtures were too liquid for proper grinding action on the paint mill. The soaps and their analyses are given in Table I. The solvents selected for consideration are given in Figure 4.

TABLE I

Analysis of Metallic Soaps

Soap	Volatile	MP	Total ash	Soluble salts	Fineness[c]
Ricinoleates[a]					
	%	°C.	%	%	%
Al, tri	.5	......	5.5	.10	gel
Ba	.2	115	25.5	....	90
Ca	2.5	95	8.5	....	65
Mg	.5	......	7.5	....	....[d]
Zn	.2	95	12.5	.50	90
Stearates[b]					
Al, tri (No. 132)	.5	113	5.5	.10	95
Ba	.2	145-155	22.5	.10	100
Ca	2.0	169	9.0	.25	100
Mg	.5	159	8.0	.35	100
Zn, (Tech.)	.5	125	15.0	.10	100

[a] Supplied by The Baker Castor Oil Company.

[b] Obtained from Witco Chemical Co. These metallic stearates are commercial grade soaps and are understood to be prepared from double-pressed stearic acid or its equivalent.

[c] Percent through 200-mesh sieve.

[d] Coarse white granules.

On standing the dispersed metallic soaps mixes exhibited a very wide range of solubility behavior ranging from clear liquids or clear gels to watery slurries or opaque crumbly gels. In many cases liquid separation occurred. In other cases the soap was incompletely wetted.

Since no convenient system appeared to be existent in the literature for describing the wide variety of solutions, gels, pastes, slurries, viscous liquids, and so forth which resulted from dispersing the soaps in different solvents, a simple scheme was proposed and used for coding the soap solutions obtained. This system covered the two properties of appearance (clarity and color) and consistency (viscosity). Limited soap swelling frequently occurred, as indicated by a separation of the mixture into a swollen soap phase and a liquid (solvent) phase. Although qualitative in nature, the coding system served to nicely describe the test results observed.

Appearance	Consistency
C Transparent (clear to straw)	1. Thin Watery Liquid
T Translucent (yellow to brown)	2. Viscous Liquid
W Opaque (white)	3. Grease, Paste, Soft Gel
	4. Hard or Crumbly Gel
	4R. Rubbery Gel

Thus the following conditions might be coded as follows:

Clear Thin Liquid	C1
Opaque Slurry	W1
Clear Hard Gel	C4
Translucent Grease	T3
Heavy Cream	W2

Using this coding, initial results were tabulated and reviewed. An inspection of the data revealed the two obvious facts that a) metallic ricinoleates are generally more soluble than stearates and b) limited soap swelling in solvent is quite common as indicated by the high incidence of two-phase systems.

This last observation pointed up the need for a more quantitative type of information which would take into account the separation of liquid from the swollen soap phase.

Hence a further and more detailed study was carried out, designed to determine the solubility and limiting swelling concentration of the metallic ricinoleates in the selected solvents.

By limiting swelling-concentration (LSC) is meant that borderline concentration of soap in solvent beyond which no further swelling or acceptance of solvent by soap takes place. Proceeding from pure soap to this LSC, the soap swells and imbibes all solvent completely with no excess solvent left over; beyond the LSC, swollen soap and saturated soap solution coexist together as a two-phase system.

In this second part of the study only aluminum stearate was included as a reference metallic soap since the preliminary screening study had shown the barium, calcium, magnesium, and zinc stearates, in general, to be both relatively insoluble and resistant to swelling action, *i.e.*, gave mostly opaque slurries, sludges, and pastes.

In obtaining a LSC, the following technique was used. A series of soap/solvent mixtures were prepared for a given test soap in a selected solvent at a number of stepwise soap concentrations (say 10%, 20%, 30%, 40%, 50% 60%).

These mixtures were then heated with stirring to just above the M.P. of the soap, if this was possible, or at the B.P. of the solvent to effect a solution of the soap. The mixture was then allowed to return to room temperature. On standing a week, those mixtures which exhibited synaeresis usually gave a clean-cut two-phase separation, consisting of soap (at its LSC) and excess of solvent; those mixtures with concentrations above the LSC appeared as homogeneous soap gels or incompletely wetted soap with no free solvent.

For the metallic soap solvent systems which failed completely to show any separation of soap from solvent, the nature of the dispersed soap at several selected percentage compositions was observed and reported. Even in those few cases where separation might have been forced, as by centrifuging, this was not done.

Because of the wide range of melting points of the soaps and the even wider range in boiling points of the solvents, this procedure was made somewhat more flexible than prior screening procedures. For example, in the case of those solvents which boiled at temperature below the melting point of the soap the boiling point of the solvent fixed the maximum dispersion temperature, and hence to achieve a hot soap solution in such cases heating and agitation were continued longer than in those cases where the soap melted.

Procedure for Determining the Solubility and Limiting Swelling Concentration of Metallic Soaps

For each determination the total weight of soap and solvent was made equal to 100 g. For 5% solution five g. of soap and 95 g. of solvent were used; for a 10% solution, 10 g. of soap and 90 g. of solvent were used, etc. The actual procedure follows:

a) The required amount of soap and solvent, totaling 100 g., was placed in a tared 250-ml. beaker.
b) The beaker was partially immersed in an oil bath.
c) The temperature of the oil bath was then adjusted to heat the soap/solvent mixture to the melting point of the soap or the boiling point of the solvent, whichever was lower.
d) The mixture was stirred thoroughly by hand at the selected temperature until a uniform product was obtained.
e) The beaker and soap solution were then reweighed, and any solvent loss was replaced.
f) After a final stirring to achieve a homogeneous product, a 50-ml. test tube was filled with the uniform dispersion to a predetermined volume and stoppered.
g) The stoppered test tubes were placed in a rack and observed after aging one week. The volume of the soap phase was estimated for all those mixtures where phase separation occurred. Where stable dispersions of swollen soap in solvent resulted instead, the gradations of behavior within the dispersion range were observed, estimated, and recorded at selected concentrations.

By lining up the several test tubes containing the several mixtures in proper sequence, where liquid separation occurred, and then by plotting the estimated volume of each soap phase against the soap concentration, it was possible to determine an approximate LSC a borderline soap concentration separating those concentrations with excess solvent and those with excess soap, *i.e.*, concentration where the soap was incompletely swollen.

A shorthand or graphic method of expressing the data obtained was adopted as a handy and concise means for describing the observed results. This notation, which is illustrated in Figures 1, 2, and 3, is self-explanatory.

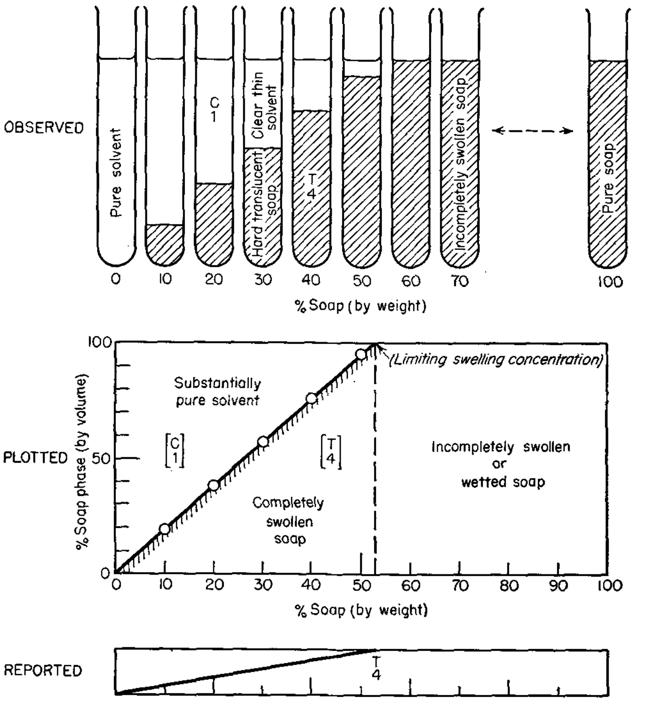


FIG. 1. Method for obtaining and reporting limiting swelling-concentration (phase separation with negligible soap solubility).

Figure 1 illustrates the type of limited swelling which normally occurs in most of the cases where phase separation takes place. In such cases the metallic soap can be considered (for all practical purposes) as substantially insoluble in the solvent. By the same token the liquid phase which separates out on cooling and standing can be considered as substantially pure solvent.

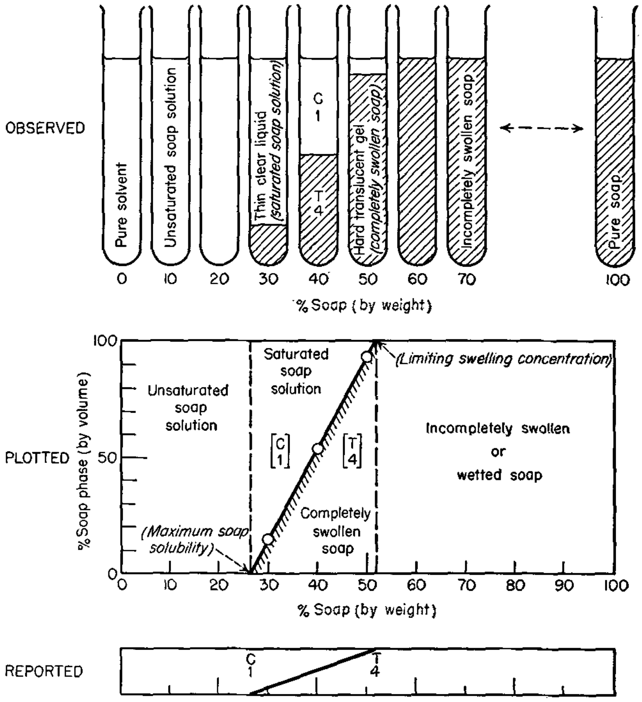


FIG. 2. Method for obtaining and reporting a) limiting swelling-concentration and b) maximum soap solubility (phase separation with significant soap solubility).

Figure 2 illustrates the few scattered instances where a significant soap solubility occurred along with phase separation. In such instances the soap solubility can be roughly gauged by reference to the intercept of the slant line with percentage scale (opposite end from the LSC intercept).

In certain cases a haze or minor precipitation occurred which was presumably due to insolubility of the non-ricinoleate fractions of the castor oil fatty

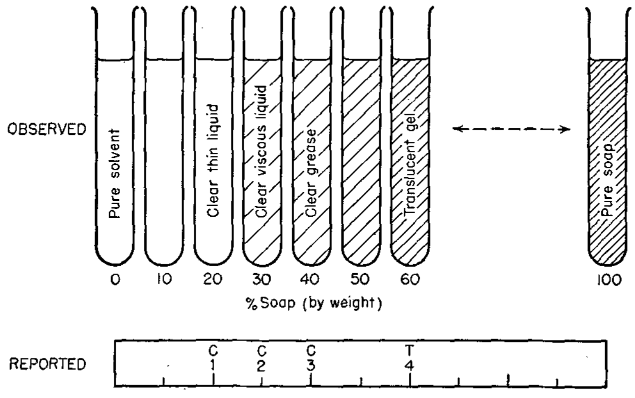
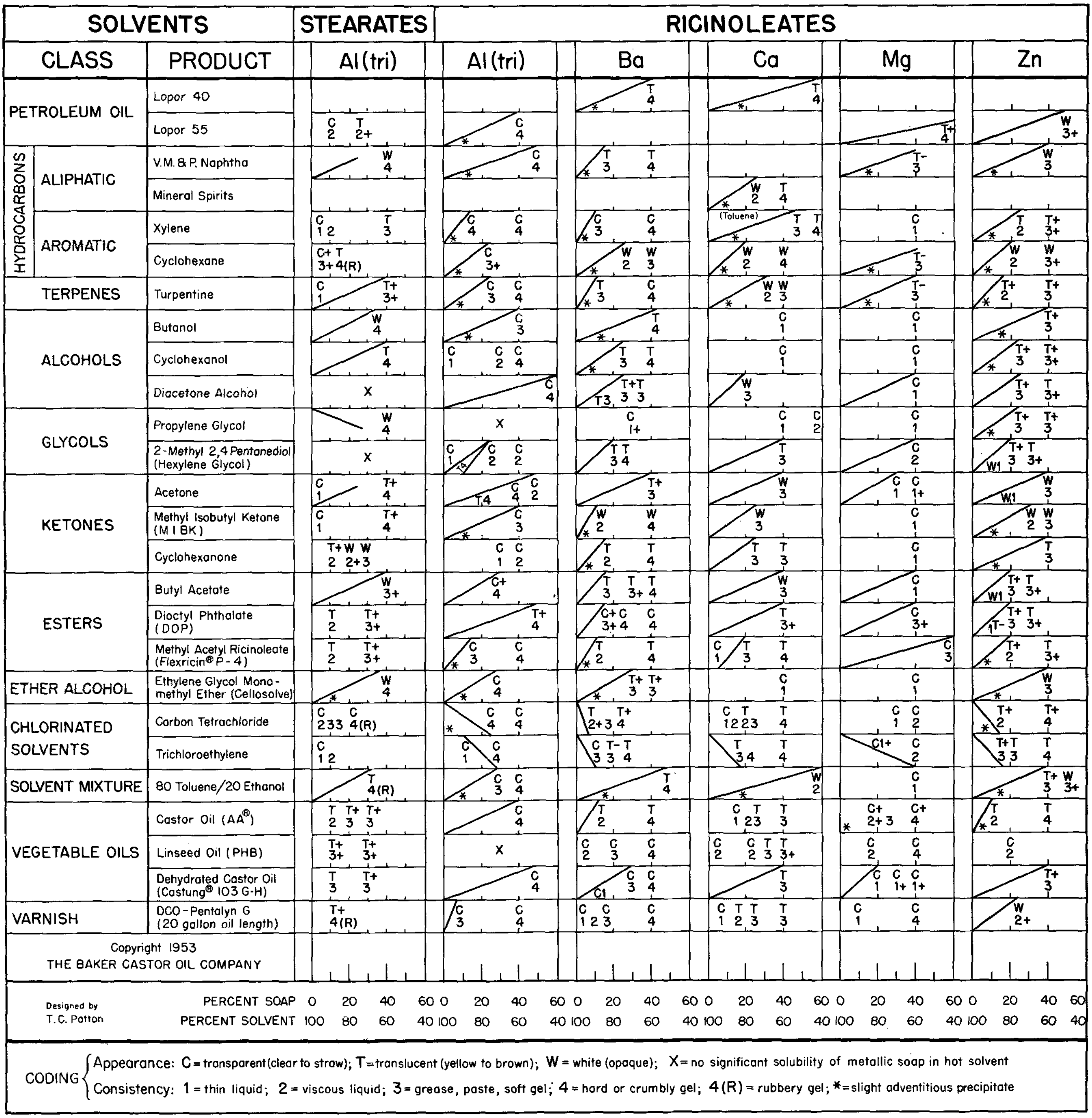


FIG. 3. Method for reporting an homogeneous type of soap dispersion at varying soap concentrations (no phase separation).



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Designed by
T. C. Patton

CODING
Appearance: C = transparent (clear to straw); T = translucent (yellow to brown); W = white (opaque); X = no significant solubility of metallic soap in hot solvent
Consistency: 1 = thin liquid; 2 = viscous liquid; 3 = grease, paste, soft gel; 4 = hard or crumbly gel; 4(R) = rubbery gel; * = slight adventitious precipitate

FIG. 4. Solubility and swelling of metallic soaps.

acids. Where this was observed, a notation was made to this effect, but the effect of any such precipitation was neglected in working out an LSC. It was felt that this action was justified since the effect of the nonricinoleate fraction was slight or negligible.

Figure 3 illustrates the method used for recording the data where no phase separation occurred, the mixtures increasing gradually in consistency from clear solvent to soap with no intermediate stage giving phase separation up to the 60% maximum soap concentration worked with in this study.

As can be seen from this shorthand graphic recording, the presence of a slant line always indicates phase separation whereas the absence of the slant line indicates the absence of phase separation, the soap remaining completely dispersed in the solvent at all soap concentrations.

The summary of final results is given in Figure 4 for some 150 soap/solvent combinations, which required preparation of well over 1,000 test solutions.

The following conclusions are drawn from a consideration of the extensive data developed by this investigation:

a) Almost without exception, aluminum tristearate and the ricinoleate soaps of aluminum (tri), barium, calcium, magnesium, and zinc are dispersible in 24 common solvents, where such soap/solvent systems are heated to just above melting point of soap or to the boiling point of the solvent (whichever is lower).

b) Of the above soap/solvent mixtures which are dispersible hot, there results, on cooling and aging for one week at room temperature, a two-phase system (consisting of swollen soap and solvent) in about 80% of the cases and a homogeneous system in about 20% of the cases.

c) In the case of the two-phase swollen-soap/solvent system a) the swollen soap appears to have a limited swelling ability, in that, beyond a critical soap concentration (a limiting swelling concentration), no further soap swelling occurs and b) the solubility of the soap in the solvent is generally very slight (on the order of less than 1%).

d) In the case of the homogeneous one-phase system there occurs a gradual increase in the consistency or body of the solvent as soap is added to it, with no intermediate stage where liquid separation takes place (at least up to the 60% maximum soap concentration employed in this study).

e) Magnesium ricinoleate is the most soluble of the six metallic soaps, eight solvents dissolving this soap up to a 40% soap concentration and beyond to give clear, thin, soap solutions. Calcium ricinoleate is the next most soluble soap.

f) Aluminum (tri) and magnesium ricinoleates tend to give clear soap/solvent mixtures whereas the other four soaps tend to give mostly translucent mixtures. Aluminum (tri) ricinoleate, with only few exceptions, swells to give clear, hard gel structures with limited swelling, whereas magnesium ricinoleate tends to give clear, thin to viscous, solutions.

g) Whereas the metallic stearates as a class, with the exception of aluminum tristearate, show a pattern of general inertness in solvents, the metallic ricinoleates show a wide pattern of solubility and swelling behavior, ranging from clear thin solutions to hard gels. In comparison with aluminum (tri) stearate, the metallic ricinoleates generally show either an equal or more extensive solubility or swelling action, and definitely a more varied behavior.

h) As anticipated, the metallic ricinoleates as a class exhibit marked solubility or swelling action in alcohols, ether-alcohols, and glycols as opposed to the marked insolubility and non-swelling of the metallic stearates, including aluminum (tri) stearate, in these hydroxy-type solvents.

i) One fact of practical significance is that a) fatty-oil type vehicles and b) hydroxy-containing liquids can generally be bodied to produce clear liquids of any viscosity by the proper use of a suitable metallic ricinoleate.

REFERENCE

1. Doss, M. P., "Properties of the Principal Fats, Fatty Oils, Waxes, Fatty Acids and Their Salts," The Texas Company, N. Y. City (1952).

[Received March 3, 1953]

Determination of Moisture in Peanut Butter

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THE moisture content of peanut butter is relatively low (6) as a result of the roasting operation. It is important to know the moisture contents of roasted peanuts and of peanut butter in order to calculate a materials balance during the processing of peanut butter, or to determine the amount of shrinkage that occurs from loss of moisture. Moisture content is particularly important in the calculation of uniformity of incorporation of stabilizers in peanut butter, in consideration of the fact that peanut butter is often stabilized by the addition of as little as 0.8% of hydrogenated peanut oil, an amount smaller than the amount of moisture present in the peanut butter. It also is important to know the moisture content of stored peanut butter because of the undesirable effect of high moisture on product quality.

At the present time there is no official method for the quantitative determination of the moisture content of peanut butter. The Official and Tentative Methods of Analysis of the American Oil Chemists' Society describe two oven weight-loss techniques (1a, b) for the determination of moisture and volatile matter in peanut kernels. Original moisture and volatile matter on the sample as received is determined by the loss in weight on heating a 40-50-g. whole kernel sample for three hours at 130°C. (designated Ab 2-49). The second method (designated Ab 3-49) is used in the determination of oil and ammonia. It consists of heating a 40-50-g. whole kernel sample 20 minutes at 130°C., followed by slicing the complete sample and then heating a 5-g. portion for two hours at 130°C. The two methods are designed to lower both materials, the whole kernel sample and the sliced, partially dried sample, to the same state of dehydration. Inasmuch as peanut butter and roasted peanuts are partially dried, the second method was considered more appropriate for the determination of moisture and volatile matter in these materials.

During an investigation of the manufacture of peanut butter at the Southern Regional Research Laboratory, Morris, *et al.*,[3] found differences in moisture content of 0.2-0.6% as determined by the forced-draft oven method for "second" moisture between the blanched, roasted peanuts and peanut butter made from such peanuts. Since the product was heated little in passage through the grinder, it was considered doubtful that the lower moisture content of the peanut butter indicated a real loss of moisture but rather that the method used was inadequate for peanut butter.

Hoffpauir (4) has pointed out that the determination of moisture content of biological materials by loss-in-weight on heating is an entirely empirical procedure, governed by temperature of heating, time of exposure, surface area of the sample, pressure, and nature of the material. It is a matter of common experience that different moisture contents are obtained for the same material on use of different methods. Without doubt such results are produced by differences in methods which impose more or less drastic conditions and hence result in greater or less loss of volatile matter from the sample. Hoffpauir's results (4) indicate that a more drastic set of conditions produces a higher apparent moisture content.

The methods of Bidwell and Sterling (2), Dean and Stark (3), and various refinements of these methods for the determination of moisture by toluene distillation have been used frequently. The improved apparatus of Tryon (5) for use with this type of method appeared to offer advantages in the determination of moisture in peanut butter, particularly in consideration of its applicability to materials of low moisture

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[3] Unpublished data.