Solubility Tests of Castor Oil

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CASTOR oil, as is well known, is completely soluble in alcohol, while all other vegetable fats are practically insoluble. Based on that fact, one of the most obvious and simple tests for the purity of castor oil is the determination of the solubility of a sample of the oil in alcohol. Various specifications for the test have been given by different authorities, using various proportions of oil and alcohol, and varying strengths of alcohol.

Thus the U. S. Pharmacopoeia IX. Edition, page 299, specifies equal volumes of 95% alcohol and castor oil. The Signal Corps U. S. A. specifications are four volumes of 90% alcohol to one of oil. Still others require that one part of oil shall be soluble in two parts of 90% alcohol and again in two parts of 95% alcohol. All authorities require complete solubility in dehydrated alcohol in all proportions. Lewkowitsch also gives (see Technology of Oils, Fats and Waxes, Fifth Edition, Vol. II, page 399) the following: "It also dissolves at 15°C in two volumes of 90%, and in four volumes of 84% alcohol. For the rapid examination of castor oil (by custom house officers) Finkener recommends agitation of 10 cc. of the sample with 50 cc. of alcohol, of the specific gravity of 0.829 at 17.5°C, in a graduated cylinder."

While these solubility tests are very valuable, too much stress should not be laid upon them. If the oil dissolves in the alcohol, it is very probably pure. If, however, the oil does not dissolve, particularly in the weaker alcohols, weaker than 95%, it should certainly not be rejected outright as impure, but should be subjected to further analysis for confirmatory proof of its purity or adulteration. In other words, the solubility tests are only sorting tests, with further investigations being needed before an oil can be rejected as impure.

We received samples of oil from four tank cars in 1919 which refused to pass either the Finkener or 90% alcohol solubility tests, analysis of which resulted as follows:

Analyses of Castor Oils which did not pass Finkener Test:

Characteristics	*A*	*B*	*C*	*D*
Sp. gr. at 15.5°C	0.9608	0.9611	0.9607	0.9613
Iodine No. (Wijs)	86.7	87.4	88.3	87.8
Sap. No.	183.6	182.8	182.3	183.2
Refraction at 15°C			1.4801	1.4805
Viscosity (130°F)			476	480
Free Fatty Acids			2.26%	2.12%
Acid Value			4.5	4.2
Halphen Test			Neg.	Neg.
Acetyl value			148.3	145.0
Solubility Tests:				
Glacial Acetic Acid			Clear	Clear
Absolute Alcohol (All proportions)			Clear	Clear
95% alc-1:2	Clear	Clear	Clear	Clear
90% alc-1:4	Turbid	Turbid	Turbid	Turbid
Petroleum Benzinc			Clear	Clear
Finkener Test 1:5.	Turbid	Turbid	Turbid	Turbid

"C" and "D" particularly could not be classed as impure oils, as most all other vegetable oils have very small acetyl values, none exceeding 30.

Sometime later a single tank car shipment of oil was tested by the Finkener method for its solubility in alcohol, and gave a turbidity. The laboratory making the test drew the conclusion that the oil was not pure, and so reported. The question was then placed before the Bureau of Chemistry for decision. Two gallon samples drawn from the shipment by two different sampling agencies, one drawn at point of origin, and one at destination, were received in the summer of 1920. The first sample was analyzed immediately and the second was held and tested ten months later. Below are given the results of the analysis:

Characteristics of a Castor Oil Fresh and 10 Months Later

	No. 1 Fresh	*No. 1 after 10 months*	*No. 2 after 10 months*
Appearance	Clear		Clear
Odor	Castor oil		Castor oil
Color	Good		Good
Sp. Gr. 15.5°C	0.9602		0.9614
I. No. (Wijs)	89.2		89.3
Sap. No.	181.1		181.2
Acid No.	6.4		6.9
Free fatty acids	3.20%		3.47%
Unsap. Fat	0.58%		0.60%
Refraction 15.5°C.,			1.4808
Viscosity 130°F.	465		473
Viscosity 212°F.	93		95.5
Acetyl No.	148.5		146.2
Sap. No. Acetylated Oil			302
Acid No. Ins.			178.9

	No. 1 Fresh	*No. 1 after 10 months*	*No. 2 after 10 months*
Neutralization No. of F. A.			179.7
Unsapon. in F. A.			0.64%
Halphen Test			Negative
Villavechia Test			Negative
Solubility Tests:			
Petroleum Ether	Clear	Clear	Clear
Glacial Acetic (All Pro.)	Clear	Clear	Clear
Abs. Alcohol (All Pro.)	Clear	Clear	Clear
95% 1:2	Clear	Clear	Clear
90% 1:2	Clear	Turbid	Turbid
90% 1:4	Clear	Turbid	Turbid
Finkener Test 1:5	Turbid	Turbid	Turbid

[1] Viscosity made by Saybolt Universal Viscosi-meter.

It will be noticed that between the time of the two analyses some changes had occurred. The specific gravity had increased .0012 the free fatty acids 0.27, and the viscosity at both temperatures showed a slight increase. Further, whereas the oil passed all the various specifications for the alcohol solubility tests except the Finkener in the first analyses, the second sample was, also, not completely soluble in the 90% alcohol. The original sample, upon retesting at the time of analyzing the second sample, showed the same failure to pass the Finkener and 90% alcohol solubility tests, although it passed the 90% test at the time of the first analysis. As stated by Lewkowitsch in Volume II, page 396 of the Fifth Edition of his Technology of Oils, Fats and Waxes, castor oil does not dry, but it does thicken. This is borne out by the increase in the gravity and viscosity while the iodine value remain unchanged. This thickening may possibly be due to a slow polymerization of the molecule. This is borne out not only by the analysis of the second sample, which had been held a year, but also by the fact that the first sample also had changed the same way, it having passed all but the Finkener test at the time of the first analysis, but showing the same turbidity in 90% alcohol as the second sample when tested ten months later.

Inasmuch as the samples pass all other requirements for pure castor oil, it did not seem that the oil could have been adulterated but that the incomplete and slowly increasing insolubility was due to some inner change of the molecule. This is all the more evident when it is remembered that all oils other than castor oil have very low acetyl values, so that even a 5% contamination with other oils would have reduced the acetyl value below 140, whereas both of the samples showed normal values of 148.0 and 146.5, respectively. Further the portions insoluble in the various alcohols as given above were completely soluble in 95% alcohol, thus offering further proof that the insoluble portion was not vegetable oils, but more probably castor oil.

At the suggestion of I. F. Laucks, we obtained further proof of this theory. A large quantity of the oil was treated with the alcohol, and the insoluble portion was allowed to settle out. This insoluble portion was freed completely from alcohol and water and a portion tested for its acetyl value. Inasmuch as all other oils have values of less than 30 for acetyl value, this insoluble fraction would have a very low acetyl value if the oil had been adulterated. The value as determined, however, was 136, proving conclusively that the insoluble portion was hydroxylated and therefore castor oil and not any other vegetable oil. This acetylated residue also showed an iodine value of 79.4, which is about what would be expected.

We therefore believe that failure to pass the solubility tests for castor oil especially those specifying alcohol of less than 95% strength should not be considered as proof of adulteration, but rather as an indication that further chemical investigation of such a sample is needed to prove or disprove its purity.

Further, while all authors state that the filtration and distillation methods of determining the acetic acid liberated from acetylated oil, give the same results, we have been unable to obtain concordant results by the filtration method. The results are always variable and low. Even if the liquid is cooled before filtering, a loss results. This is probably due to the volatilization of the acid. However, distillation, especially if phosphoric acid is used for acidulating instead of sulphuric acid always gives concordant, and consistent results. This method is used for determining the acetic acid in calcium acetates, and we have found it much better for determining the acetyl value than the use of sulphuric acid. If the liquid being distilled is allowed to concentrate to a volume of 50 cc. or less, the sulphuric acid is liable to char the acetylated oil (particularly that material which spatters the sides of the flask above the liquid), and liberates volatile acids which go into the distillate and vitiate the results. By using phosphoric acid, that danger is obviated and we can obtain consistent results with good checks, whereas by the filtration method we obtained six different values ranging from 125 to 143 on a sample of medicinal castor oil of known purity, and with a true acetyl value of 148 as determined by the distillation method.

Our method is as follows:

Boil gently 20 gr. of filtered dry oil with 20 cc. of acetic anhydride and 10 grams of anhydrous sodium acetate in a round-bottomed 150 cc. flask (attached to an air-jacketed reflux condenser) for two hours, allowing no material to cake on the sides. Cool somewhat and before breaking connections rinse down the condenser with water, adding about 50 to 80 cc. of water. Pour the contents of the flask into 500 cc. of water in a large beaker and boil for 30 minutes, using glass beads or a stirring rod reaching the bottom of the beaker to prevent bumping. Siphon off the water and boil the oily layer with fresh water until the wash water is no longer acid to litmus. Separate the acetylated fat from the water, filter and dry in an oven at 100°C.

Weigh 2-4 grams of the acetylated fat into a 500 cc. Erlenmeyer flask, add 50 cc. of alcoholic potash (40 grs. to the litre) and saponify for one hour. Evaporate off the alcohol and dissolve the soap in water. Fit up the usual steam distillation apparatus using a two-litre flask for the steam boiler and allow the steam to escape from the flask for 15 minutes to insure the removal of carbon dioxide from the water. Acidulate the soap solution of the saponified acetylated fat with phosphoric acid using methyl orange as an indicator, conduct the steam into this liquid, and keep both the flasks boiling. Catch the distillate from the Erlenmeyer flask in 40 cc. of quarter normal caustic solution, being careful that the caustic solution seals the end of the delivery tube. After 400 cc. have passed over remove the receiver and titrate back with acid. Continue the distillation, it not being necessary to use caustic in the receiver but being sure that the delivery tube is sealed in with water. Test each 100 cc. of distillate until not more than 0.1 cc. of quarter normal caustic is necessary to produce a red color with phenophthalein.

The total number of ccs. of quarter normal caustic used to titrate the distilled acid multiplied by 2.5 and by 5.61, and divided by the weight of sample taken, gives the acetyl value. It is better to keep the volume of liquid in the Erlenmeyer flask as small as possible during the distillation to prevent too much splashing, with its consequent carrying-over of the acid solution by entrainment.

Grading of Yellow Glasses

The complete report of the calibration of the sixty-five 35 Yellow Lovibond glasses collected from the members of the American Oil Chemists' Society and submitted to the Bureau of Standards in August, 1927 for calibration will be published in the April issue of the Bureau's Journal of Research. Copies of this paper will be sent to each member who submitted glasses. If any others desire them they can be obtained from the Government Printing Office.

In order to expedite this work the American Oil Chemists' Society employed and detailed to the Bureau of Standards in September, 1927 a research associate to assist in the standardization of glasses. The Bureau has previously examined considerable numbers of the red glasses and disclosed some irregularities of such magnitude as to be of serious consequence in comparison with the small differences which are considered in fixing the market price of the oil. The present report deals with 65 yellow glasses all of nominally the same grade designated as "35 yellow" on the British scale. The glasses were collected by the American Oil Chemists' Society mostly from among glasses in use by its members. Very few new glasses were included. These glasses were submitted to the Bureau by the Society during the month of August, 1927.

The Bureau has conducted a thorough-going, precise intercomparison of these glasses, and reports in detail the true equivalent to be assigned to each glass in using it in careful critical work. It is worthy of note, however, that the errors found in these yellow glasses are negligible in comparison with the uncertainties inherent in the customary methods of using the glasses to grade the oils. An outstanding result of the investigation is the conclusion that the discrepancies in color grading which have disturbed traders in the oils cannot be attributed to errors in the yellow glasses. The origin of these discrepancies is rather to be sought in the following factors: (a) Unstandardized and insensitive methods of comparing the colors of oil and glasses; (b) abnormal color sense and low power of hue discrimination in some users of the glasses; (c) errors in the red glasses. Only after these sources of uncertainty have been eliminated will it be worth while to take into practical account the relatively small errors in the yellow glasses.

Kellogg Quarterly Earnings

Spencer Kellogg & Sons, Inc., have issued an earnings statement for the twelve weeks ending December 22, showing net of $182,777 after all deductions, or 36 cents a share on outstanding no par common stock.