differentiate between "synthetic" and natural conjugated and non-conjugated oils or fatty acids.

Linolenic acid is the only other constituent occurring in drying oils that may cause interference through the formation of a solid conjugation product. The yield of pseudo-elaeostearic acid is small however, and it can hardly be mistaken for the solid dienoic acid.

For determining the presence of DCO fatty acids in alkyd resins Stafford and Williams (18) have recommended the use of UV-spectrometry. Since the spectrometer however allows no distinction between DCO on the one hand and a conjugated dienoic product on the other, the use of the chemical method here proposed is offered as an analytical tool for investigating alkyds.

The method might well be adapted for quantitative determination. A definite solubility of the solid 10,12-acid in the alcoholic solution at low temperature however will have to be taken into consideration. A reference curve for pure 9,12-cis,trans-linoleic acid, showing the yields of 10,12-octadecadienoic acid obtained therefrom with varying percentages present in a mixture would be desirable. Cis,trans-linoleic acid, an isomer yielding no solid bromides, has not as yet however been isolated in a pure form.

Limitation. The laboratory samples of DCO investigated here have in all cases been prepared by a catalytic procedure (20). It is not likely that all the commercial samples tested have been made with catalysts of the same type. Until the products from all industrially used processes of castor oil dehydration have been tested in this fashion however, the proposed method should be considered limited to DCO obtained by any procedure employing an acidic catalyst.

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Spectrophotometric Analysis of Tall Oil Rosin Acids

FRANK J. BALL and WILLIAM G. VARDELL, West Virginia Pulp and Paper Company, Charleston, South Carolina

TALL OIL is a by-product of the kraft paper industry which has found extensive use in protective coatings and industrial soaps for it is essentially a mixture of unsaturated fatty and rosin acids containing a small percentage of higher alcohols (28). There is annually available about 130,000 tons of the whole tall oil, and this figure is steadily growing with the expanding kraft paper industry. Depending upon demand, 40 to 60% of the whole tall oil is refined by distillation or acid refining (27).

The fatty acid and unsaponifiable fractions of tall oil have been investigated and their compositions clarified to some extent. The fatty acid portion of the whole tall oil contains approximately 45% oleic, 48% linoleic, and 7% palmitic acid (1). In the unsaponifiable portion substantial quantities of β-sitosterol and lignoceryl alcohol have been identified (19).

Investigation of the rosin acid fraction of tall oil has been retarded by the confusion which has existed until recently in the chemistry and composition of the rosin acids. It has lately been demonstrated that the rosin acids in gum and wood rosin are composed of a mixture of eight different rosin acids, whose structures are shown in Figure 1. Their approximate proportions have been found to be 30-40% abietic, 10-20% neoabietic, 14% dihydroabietic, 14% tetrahydroabietic, 5% dehydroabietic, 16% of the isomeric dextropimaric acids, and less than 1% of levopimaric acid (12). Of these acids the most significant are abietic and neoabietic acids, which are interconvertible, and which are responsible for the oxidation of rosin and the reaction of rosin with maleic anhydride in resin formation. These two acids disproportionate when subjected to heat and catalysts to yield the stable dehydrogenated and hydrogenated abietic acids.

While most of the investigations of tall oil rosin acids have been conducted on the acids crystallizing from distilled tall oil, some information has been collected on those in whole tall oil. By selective esterification Dittmer (9) isolated the total rosin acids from Swedish whole tall oil as brown crystals. Recrystallization from methanol yielded yellow crystals, which melted at 161-166°C. and analyzed for $C_{20}H_{30}O_2$, the same as abietic acid. Hasselstrom (20) likewise formed abietic acid (m.p. 164.5-165.5°C.; $[\alpha]_D - 53.9$°C.) by the action of glacial acetic acid on the material crystallizing from American whole tall oil. In neither case was any yield given. Pyhala (24, 25) isolated crystalline rosin acids from whole Finnish tall oil

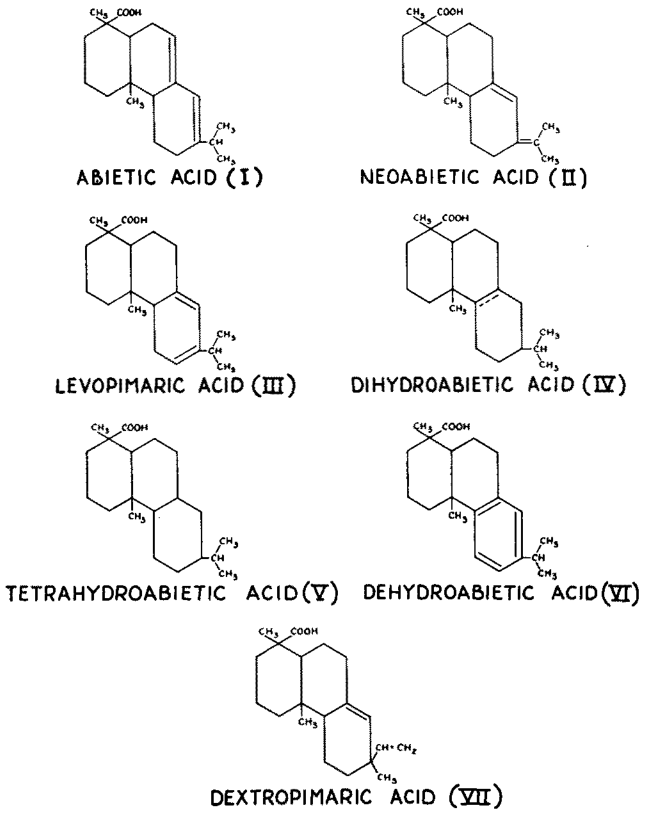

FIG. 1. Rosin acids in gum and wood rosin.

with melting point ranging from 156-158°C. to 175-180°C.; however his method of separation was not disclosed.

Several different rosin acids have been isolated and identified in the rosin acids which crystallize from distilled tall oil. Aschan (4, 5) isolated from vacuum distilled Finnish tall oil, a crystalline material with a melting point of 182-183°C., a molecular weight of 303, and an equivalent weight of 301. This "pinabietic acid" was later found to be a mixture (6, 21), and Hasselstrom identified 9% dehydroabietic acid and 5% dihydroabietic acid in the tall oil rosin from distilled Finnish tall oil (21). He also isolated from the same sample an unreported yield of crystalline acid (m.p. 163-165°C.; $[\alpha]_D - 79.9$°C. in ethanol) identical to Steele's abietic acid from wood rosin.

Sanderman (26) estimated the rosin acids which crystallize from vacuum distilled Finnish tall oil to be 25% dextropimaric, 50% abietic, and 25% pyroabietic acid, the latter probably (11, 23) consisting of dehydroabietic, dihydroabietic, and tetrahydroabietic acids. His analytical method was based on the change in optical rotation and softening point of the rosin acids under the influence of heat.

Hasselstrom (16) reported that the rosin acid crystallizing from distilled tall oil can be dehydrogenated to yield 70-80% of dehydroabietic acid while gum or wood rosin yields only 38-50% dehydroabietic acid. This would indicate that the rosin acids crystallizing from distilled American tall oil were largely of the abietic acid type and did not include much dextropimaric acid. He also reported that 60% of the rosin acids in whole tall oil were collected as dehydroabietic acid after heating the tall oil to 190-200°C. in the presence of iodine catalyst (17). The rosin acids were isolated by selective esterification, identified, and determined by sulfonation (11, 18).

Aschan (2, 3) isolated hydroxy rosin acids, termed colophenic acids, both in tall oil and in wood rosin. He believed these acids, which melted around 100°C., were oxidation products of the original rosin acids. In fact, he was able to prepare the same hydroxy acids by oxidation of his "pinabietic acid" with hydrogen peroxide. This atmospheric oxidation of rosin acids proceeds rapidly and must always be taken into account. Enkvist (10) showed oxidation proceeded during the determination of oxidized acids of tall oil by the petroleum ether insolubility test.

Harris separated the rosin acids from tall oil by preferentially precipitating the rosin acids as the amine salts of certain primary amines, such as cyclohexylamine. The free rosin acids could then be isolated in better than 95% yield by heating or acid washing the amine salt (13). Harris also stated that the tall oil rosin acids so isolated exhibited essentially the same composition as the acid fraction of gum or wood rosin (12).

Recently Harris and Sanderson reported a relatively simple spectrophotometric method of determining the amount of abietic and neoabietic acids in rosin (15). Because of the confusing nature of some of the earlier work it was felt that the application of this method to the rosin acids of tall oil and tall oil products would be a definite contribution to the chemistry of tall oil. This is especially true since abietic and neoabietic acids, known as the abietic-type acids, are important because of their reactions with oxygen and maleic anhydride.

This paper describes an investigation of the abietic-type acids in whole tall oil, distilled tall oil, crystallized rosin acids from distilled tall oil, acid-refined tall oil, and using the Harris and Sanderson spectrophotometric method.

Materials

Whole tall oil.
Commercial double vacuum distilled tall oil.
Commercial abietic acid crystallized from distilled tall oil.
Commercial acid-refined tall oil.
Commercial tall oil rosin separated by fractional distillation.
WW wood rosin.
WW gum rosin.
Disproportionated rosin soap.
Cyclohexylamine, b.p. 133-5°C.—Eastman Kodak Company.
Hydrochloric acid, C.P.—J. T. Baker Chemical Company.
Boric acid, C.P.—J. T. Baker Chemical Company.
Pure 95% ethyl alcohol—Publicker Industries Inc.

Procedure for Separation and Analysis

Since all tall oils contain fatty acids, such as conjugated linoleic acid, which exhibit absorption maxima in the wavelength range of abietic acid (8), it is advisable to remove these fatty acids prior to making a spectrophotometric analysis. The method used involves precipitation of the rosin acids in the form of cyclohexylamine salts from an acetone solution of the tall oil. This method had been shown by Harris (13) to yield about 95% of the unchanged rosin acid salt. In practice, 20 parts by weight of tall oil were weighed out and dissolved in 35 parts by weight of acetone. After chilling the mixture in an ice-bath to about 5°C., a mixture of one mole cyclohexylamine per acid equivalent of the tall oil and 15 parts of acetone was slowly added. Rapid motor stirring was maintained until the reacted mass had cooled again to 5°C., and the precipitated rosin acid salts were separated by suction filtration. The remaining traces of fatty acids and excess cyclohexylamine were removed by washing with small portions of cold acetone until the wash ran clear.

Regeneration of the rosin acids from the cyclohexylamine salts was accomplished with a boric acid wash. The cyclohexylamine salts were suspended in 100 ml. of ethyl ether and washed with successive portions of a saturated boric acid solution until all of the salts had dissolved in the ether layer. The ether layer was then washed four times with distilled water to remove traces of boric acid and cyclohexylamine, leaving the purified rosin acids in ether solution. The solid acids were recovered by boiling off the ether under vacuum at 75°C. They were then blanketed with nitrogen to prevent air-oxidation.

The spectrophotometric data was obtained on a Beckman Spectrophotometer, Type DU. The rosin acids were dissolved in pure 95% ethanol. A concentration of 15-20 mg. of rosin acids per liter gave convenient instrument range deflection. Acid isomerization of neoabietic acid to abietic acid, prior to determining the total abietic-type acids, was accomplished by refluxing under nitrogen 1 g. of the rosin acids in 10 ml. of 95% ethanol containing 0.2 ml. of concentrated hydrochloric acid. After 1.5 hours reflux the solution was diluted to the appropriate concentration for analysis.

The percentages of abietic and abietic-type acids in the tall oil rosin were calculated according to the method of Harris (15). The specific absorption coefficients at 241 millimicrons and 248.5 millimicrons were taken from the ultraviolet absorption curve for the rosin acid sample. The difference in these specific absorption coefficients was then divided by 27.5, a constant value characteristic of pure abietic acid, and then multiplied by 100 to obtain the percentage abietic acid in the sample. The content of abietic-type acids was determined in like manner except that the ultraviolet absorption curve was obtained on the isomerized rosin acid sample.

The value obtained for the abietic acid content (in the nonisomerized acids) is a minimum value, for neoabietic acid exhibits a strong absorption band at 250 millimicrons, and this raises the specific absorption coefficient at 248.5 millimicrons, thus giving a smaller difference between the coefficients at 241 and 248.5 millimicrons.

Isolation by Cyclohexylamine Salt Formation

Cyclohexylamine salt formation was used to isolate the rosin acids from whole tall oil, double vacuum distilled tall oil, acid refined tall oil, and commercial abietic acid crystals from distilled tall oil. As seen in Table I, the yield of cyclohexylamine precipitated acids is 94-100% of the total rosin acids in the sample as determined by ASTM analysis (7). These rosin acids in every case were solid and crystallized either during evaporation of the solvent or on standing under nitrogen. The cyclohexylamine precipitated acids from the double vacuum distilled tall oil contained 95% rosin acids, as determined by the ASTM method (7).

TABLE I
Rosin Acids Precipitated by Cyclohexylamine

Sample	Rosin acids in sample by ASTM analysis % of sample	Acids precipitated by cyclohexylamine	
		% of sample	% of rosin acids
Commercial abietic acid crystals from distilled tall oil	90.4	91.0	101
Double vacuum distilled tall oil	35.0	33.9	97
Whole tall oil	48.0	45.7	95
Acid-refined tall oil	52.9	49.5	94

Results of Spectrophotometric Analysis

The results obtained on spectrophotometric analysis of tall oil rosin acids show that these acids contain abietic and neoabietic acids. The presence of abietic acid in the tall oil rosin acids is demonstrated by the shape of the absorption curve (No. 3 in Figure 2), which is characteristic of abietic acid (15).

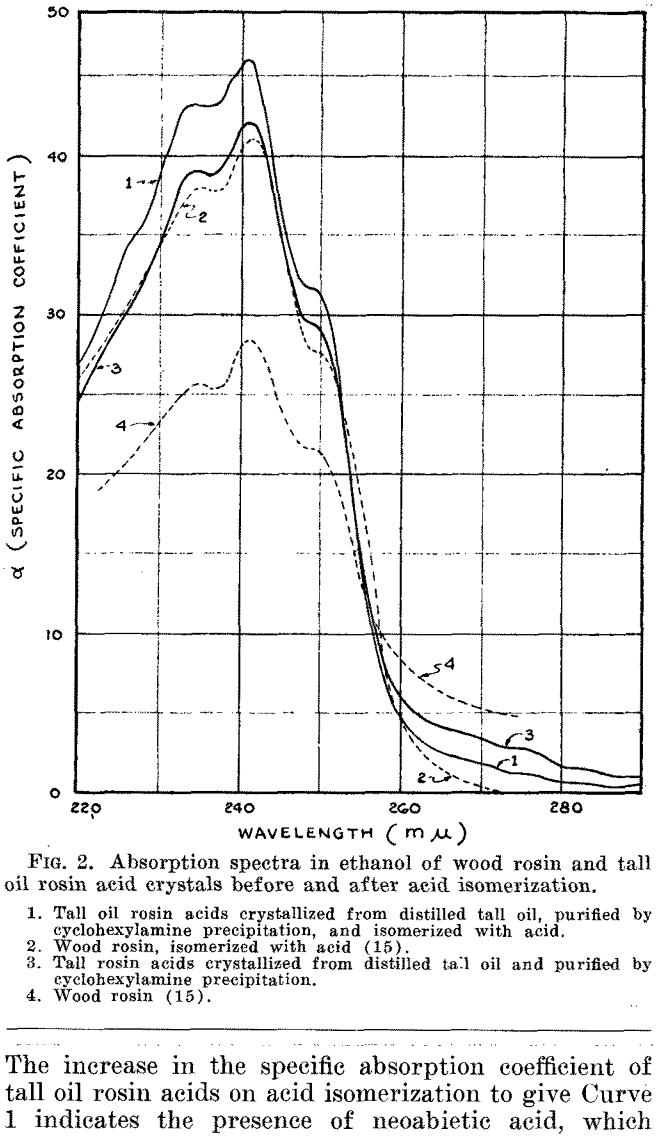

FIG. 2. Absorption spectra in ethanol of wood rosin and tall oil rosin acid crystals before and after acid isomerization.

1. Tall oil rosin acids crystallized from distilled tall oil, purified by cyclohexylamine precipitation, and isomerized with acid.
2. Wood rosin, isomerized with acid (15).
3. Tall rosin acids crystallized from distilled tall oil and purified by cyclohexylamine precipitation.
4. Wood rosin (15).

The increase in the specific absorption coefficient of tall oil rosin acids on acid isomerization to give Curve 1 indicates the presence of neoabietic acid, which isomerized to abietic acid under the acid treatment. Levopimaric acid, if it were present, could also be responsible for this increase in absorption coefficient on acid isomerization; but since all the tall oil products have been heated above 100°C. in processing, the levopimaric acid should be negligible (12). In Figure 2 the ultraviolet absorption spectra of wood rosin and tall oil rosin acid crystals are compared before and after isomerization.

On determination of the ultraviolet absorption spectrum of the rosin acids isolated from several different tall oil products, similar absorption curves were obtained. From these curves the specific absorption coefficients at 241 and 248.5 millimicrons were noted, and from these values the abietic acid contents were calculated as previously described. From similar values obtained after acid isomerization of the rosin acids the contents of abietic-type acids were calculated. The slight inflection in Curves 1 and 3 in Figure 2 at about 278 millimicrons indicate the presence of dehydroabietic acid in the tall oil rosin acids (14). No method has yet been published however to determine the dehydroabietic acid spectrophotometrically with good accuracy.

In Table II are presented the specific absorption coefficients and the calculated abietic and abietic-type acids in the rosin acids isolated from several tall oil products by cyclohexylamine precipitation.

TABLE II

Abietic and Abietic-Type Acids in Rosin Acids Isolated From Different Tall Oil Products by Cyclohexylamine Precipitation

Rosin acids source	Specific absorption coefficient				Percentage of rosin acids	
	Non-isomerized		Isomerized		Abietic acid (minimum)	Abietic-type acids
	241 mμ	248.5 mμ	241 mμ	248.5 mμ		
Whole tall oil						
Sample 1........	39.1	32.6	45.0	33.1	25	44
Sample 2........	38.4	31.6	......	......	24	....
Double distilled tall oil............	35.9	26.4	37.5	25.4	35	44
Acid-refined tall oil						
Sample 1........	35.1	25.2	34.2	25.0	35	33
Sample 2........	35.9	25.9	......	......	36	....
Commercial abietic acid crystals from distilled tall oil..................	42.2	29.6	46.0	31.7	46	52

The isolated rosin acids from whole tall oil and double distilled tall oil contain approximately the same amount of abietic-type acids. In the distilled tall oil the percentage of abietic acid is somewhat higher possibly because of isomerization of a portion of the neoabietic acid to abietic acid during distillation.

The rosin acids crystallized from distilled tall oil contain somewhat more abietic-type acids than do the rosin acids in whole or distilled tall oil. In addition about 90% of the abietic-type acids in the rosin acids recovered by crystallization consist of pure abietic acids. It appeared possible in crystallizing rosin acids from tall oil that one of the seven forms of rosin acid would crystallize preferentially and that the commercial abietic acid crystals from distilled tall oil would thereby differ fundamentally from rosin. While the results indicate that abietic acid crystallizes somewhat preferentially, the rosin acid crystals still have a composition close to the rosin acids of gum or wood rosin, as seen in Table III.

The rosin acids isolated from acid-refined tall oil exhibited a lower abietic-type acid content than whole tall oil. This is not unexpected for the sulfuric acid treatment should have polymerized some of the abietic-type acids. In addition, all of the abietic-type acids in acid-refined tall oil are abietic acid for the neoabietic acid has already been isomerized to abietic acid by the sulfuric acid treatment.

TABLE III

Percentage of Abietic and Abietic-Type Acids in Gum, Wood, and Tall Oil Rosin

Rosin	Specific absorption coefficient				Abietic acid (minimum), %	Abietic-type acid, %
	Non-isomerized		Isomerized			
	241 mμ	248.5 mμ	241 mμ	248.5 mμ		
WW wood rosin.....	37.8	29.9	43.9	30.8	29	48
WW gum rosin......	36.1	30.8	44.6	31.2	19	49
Disproportionated wood rosin.........	0.0	0.3	......	......	0	....
Commercial abietic acid crystals from distilled tall oil (90-91% rosin acids)						
Sample 1...........	41.6	29.6	43.0	30.2	44	47
Sample 2...........	43.5	30.7	......	......	45	....
Sample 3...........	44.0	31.3	......	......	46	....
Sample 4...........	42.1	29.3	......	......	46	....
Sample 5...........	47.9	33.7	......	......	51	....
Commercial tall oil rosin by fractional distillation (88% rosin acids)...............	34.9	26.2	39.0	27.8	32	41

In Table III the abietic and abietic-type acid contents of gum, wood, and tall oil rosins are compared. The results in this table show the similarity between gum rosin, wood rosin, and tall oil rosin acids. There is very close agreement in the amounts of abietic-type acids in gum rosin, wood rosin, and commercial abietic acid crystals from distilled tall oil. There is much more pure abietic acid in the crystallized tall oil rosin acids than in gum or wood rosin, but since abietic and neoabietic acids are interconvertible, it is the total of the two, the abietic-type acids, that is significant. The sample of tall oil rosin obtained by fractional distillation contained somewhat less abietic and abietic-type acids than the gum rosin, wood rosin, or tall oil rosin crystals.

For comparison, the ultraviolet absorption spectrum of disproportionated wood rosin was determined. In this product the abietic type acids originally present in wood rosin are disproportionated to hydrogenated and dehydrogenated rosin acids. As seen in Table III the disproportionated wood rosin showed no abietic acid by spectrophotometric analysis.

Discussion

The spectrophotometric results obtained in this paper indicate that, as in the case of gum and wood rosin, about half of the rosin acids in whole tall oil, distilled tall oil, or tall oil rosin acid crystals are abietic-type acids. The composition of the remaining tall oil rosin acids could not be determined by spectrophotometric means, except that the presence of dehydroabietic acid was indicated by an inflection in the absorption curves around 278 millimicrons.

Earlier reports that half of the tall oil rosin acids are liquid rosin acids (22) appear to be in error or to depend on the method of separation. With the milder isolation method used in this study the rosin acids were obtained in all cases as solids which crystallized. The rosin acids in acid-refined tall oil contain somewhat less abietic-type acids than those from whole tall oil and probably correspond more to the rosin acids in polymerized rosin.

Summary

About half of the rosin acids in whole and distilled tall oil consist of abietic and neoabietic acids, as distinguished from hydroabietic acids, dehydroabietic acid, and the pimaric acids. In this respect the tall oil rosin acids are similar to those from gum or wood rosin. This was established by spectrophotometric analysis of the rosin acids from whole tall oil, double distilled tall oil, rosin acids crystallized from tall oil, and rosin acids separated from tall oil by fractional distillation. The rosin acids crystallized from tall oil contained the highest percentage of abietic acid, but the sum of abietic and neoabietic acids was only slightly higher.

The rosin acids from acid refined tall oil contained appreciably less abietic and neoabietic acid than the others.

Before spectrophotometric analysis the rosin acids were isolated from the tall oils in about 95% yield by cyclohexylamine precipitation.

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Acetone Numbers of Thermally Polymerized Drying Oils[1]

OLIVER GRUMMITT, ALBERT ARTERS, and JAMES STEARNS,
Sherwin-Williams Company, Cleveland, Ohio[2]

THIS investigation of acetone numbers of bodied drying oils is part of a program to develop tests and analytical methods in order to correlate the properties of these oils with their performance as coating vehicles. Specifications on a bodied oil frequently give only the kind of oil, viscosity, acid number, and color, but it is well known that oils having essentially the same specifications may produce paints and varnishes of widely different properties. This variation may be due to unknown differences in composition. Bodied oils consist of varying proportions of monomeric glycerides, polymeric glycerides, and decomposition products, both acidic and neutral. Tests and analytical methods which measure or reflect these components should be useful in predicting the vehicle properties of the oil.

The acetone number is defined as the quantity of acetone, expressed in grams per 100 g. of oil, which is required to produce a permanent cloudiness in the oil at 25°C. (2, 4, 6). It is a quantitative measure of the well-known property of bodied oils of becoming less soluble with increasing viscosity. Related to this determination is the acetone extract (5, 7), the acetone point (8), and the Behr process of extracting the unpolymerized portion of bodied oils with acetone (3).

One would expect the acetone number to be a function of the relative amounts of monomeric and polymeric glycerides and of the nature of the polymer, particularly its molecular weight distribution and degree of cross linking. Such information should aid in understanding the behavior of bodied oils as vehicles.

Experimental

The procedure given here is based on the published methods (2, 4, 6). In several respects it is believed to be an improved method.

Anhydrous acetone is made by allowing 1.5 l. of reagent grade acetone and 200 g. of anhydrous calcium sulfate (Drierite) to stand in a 2-l. r.b. flask with standard taper joint, protected with a drying tube, for three days with occasional shaking. About 70% of the acetone is distilled directly from this flask and the drying agent in a dry all-glass apparatus into the dry bottle of an automatic burette apparatus.[3] The bottle is protected with a drying tube to prevent moisture from entering during distillation. The clean, dry burette with its drying tubes is fitted to the bottle.

To check the water content of the acetone its specific gravity at 25° C./25° C. is determined with a calibrated g.s. 50-ml. volumetric flask. Values in the range of 0.7864-0.7872, which indicate a water content of 0.00-0.24%, show that the acetone is satisfactory. A standardization procedure for checking the acetone is described below.

Duplicate 30-g. samples of oil, weighed to the nearest 0.01 g., are weighed into clean, dry 250-ml. Erlenmeyer flasks. A rubber nipple is slipped over the mouth of the flask and the flask is immersed in a constant temperature water bath so that the water level is about 1 in. above the oil sample. The bath is held at 25 ± 0.1°. After allowing at least 15 minutes for the sample to reach 25°, the tip of the burette containing acetone is inserted through the nipple.

The flask is swirled gently while acetone is added

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[2] Address: Sherwin-Williams Laboratory, Western Reserve University, Cleveland 6, O.

[3] The water jacket for the burette as described in the A.S.T.M. method (2) is not considered to be necessary if the titration is done as specified here. The excellent reproducibility is evidence for this statement (*v.i.*).