blue oxide of tungsten, suffers no decomposition at temperatures up to 400°. A trace of moisture, however, causes decomposition and the evolution of hydrogen sulfide.

9. In the presence of any of the three metallic oxides employed as catalysts, a mixture of absolute alcohol and carbon disulfide produced considerable quantities of ethyl mercaptan. Titanium dioxide, which had been almost without action upon alcohol alone, proved the most active catalyst for this esterification. This new method may be advantageous for the synthesis of certain mercaptans.

10. From alcohol and carbon disulfide, amounts of high-boiling liquids were obtained, but in quantities too small for identification. We obtained no other evidence of the formation of esters of thiocarbonic acids by interaction of alcohol and carbon disulfide.

NEW HAVEN, CONNECTICUT

ABIETIC ACID AND CERTAIN METAL ABIETATES[1]

BY LAWRENCE L. STEELE

Introduction

Abietic acid is the name most commonly given to the crystalline material made by treating ordinary rosin with alcohol or other organic solvents. Many years ago Maly[2] expressed the view that rosin was essentially the anhydride of abietic acid, but his idea has not been generally accepted. Recently Knecht and Hibbert[3] have presented strong evidence in favor of the anhydride theory for rosin. From the assumption that rosin is an acid anhydride, a new method for the preparation of abietic acid has been developed by which a pure product can be made more easily and in larger yield than by the older published methods. Some physical and chemical data of the product will be given together with a description of the preparation of several metallic abietates with their analyses for metal content.

Methods for the Preparation of Abietic Acid

The method of Maly[4] has been used extensively for preparing abietic acid. Rosin is heated with 70% alcohol, whereby after some hours it partly dissolves and partly crystallizes. The impure crystals are treated in the same way with dil. alcohol a number of times and finally repeatedly recrystallized from strong alcohol. The method is tedious and the yield of pure product is very low.

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[1] Published by permission of the Director of the Bureau of Standards.

[2] Maly, *Ann.*, **149**, 244 (1869).

[3] Knecht and Hibbert, *J. Soc. Dyers Colour.*, **35**, 150 (1919).

[4] Maly, *J. prakt. Chem.*, **86**, 111 (1862).

Levy[5] fractionally distilled rosin in a vacuum and crystallized the distillate from methyl alcohol. The product melted at 178–182° and was probably an isomer of the acid prepared from rosin without distillation.

Cohn[6] heated powdered white rosin with methyl alcohol and a small proportion of strong sulfuric acid. The mixture partly solidifies to an impure crystal mass of abietic acid which is washed and recrystallized from pure methyl alcohol. The product by this method is liable to be contaminated with a yellow impurity, hard to remove, probably formed by the action of the sulfuric acid upon impurities in the rosin.

Knecht and Hibbert[7] dissolved rosin in glacial acetic acid and allowed the solution to stand for a week, whereby abietic acid separated and was filtered off and recrystallized approximately 20 times from acetic acid, methyl alcohol and ethyl alcohol. This method is tedious and the yield of pure product is low.

Description of a New Method for the Preparation of Abietic Acid

If the view that rosin contains abietic anhydride is accepted, it follows that in all the methods for the isolation of abietic acid from rosin, the process is essentially one of hydration. The fact that rosin is hydrated by a solvent containing water was proved by the following experiments. In 2 flasks equal weights of rosin were dissolved by heating in approximately the same weight of 98% acetic acid. One flask was then set aside while the contents of the other flask were boiled vigorously under a reflux condenser for 2 hours. The contents of both flasks were then brought to room temperature and a few crystals of abietic acid added to each flask. In a short time crystallization started in the flask which had been heated for the period of 2 hours and after several hours this flask was nearly filled with crystals. The contents of the other flask did not crystallize to an appreciable extent, even after standing for 3 days. It was evident that the rosin was hydrated by heating with the 98% acetic acid. The following method for the preparation of abietic acid from rosin was developed after a series of experiments.

Seven hundred g. of white rosin (WW or WG grade) in small lumps[8] was boiled with 500 cc. of 98% acetic acid for 2 hours under a reflux condenser. The mixture was then filtered while hot through a large plaited filter paper and the filtrate cooled to room temperature or lower. A few crystals of abietic acid were added to start crystallization or, when none of this product was available, the solution was allowed to stand overnight, this whereby spontaneous crystallization took place. If the solution was "seeded" with abietic acid, it usually started to crystallize within an hour and the liquid became a solid mass of crystals after standing overnight. The product was filtered on a Büchner funnel with suction and the filtrate set aside for a second crop of crystals. The material on the filter was

[5] Levy, *Z. anorg. Chem.*, **18**, 1739 (1905).

[6] Cohn, *Chem. Ztg.*, **40**, 791 (1916).

[7] Ref. 3, p. 151.

[8] Rosin which has stood in powdered form for considerable lengths of time becomes partially oxidized and is unsuitable.

sucked as free from mother liquor as possible and washed with successive portions of cold alcohol (9 parts by volume of 95% ethyl or denatured alcohol to one part of water) until the filtrate was practically colorless.

The yield of air-dried product was usually about 350 g., counting the second crop of material recovered from the mother liquor. Some of the product, prepared as above, was placed on a bit of porous porcelain plate and washed with a little strong alcohol. This material when dried and powdered showed a melting point of 155–159°. Some of the product was recrystallized from 95% alcohol and then was found to melt at 158–162°. These crystals had been washed thoroughly with the dil. alcohol and dried in a vacuum before the melting-point determination was made. A material of melting point 161–165° resulted from a second crystalliza-tion in the same manner, while after a third crystallization, the product was unchanged in melting point.[9]

The melting-point determinations were made with a totally immersed calibrated thermometer by the common capillary-tube method. A rate of heating of approximately 1° rise per minute was used, the sample being introduced into the bath at a temperature of 150°.

Glacial acetic acid (98%) was found to be more efficient than alcohol for recrystallizing impure abietic acid. For example, 100 g. of the crude acid was dissolved by heating in 100 cc. of acetic acid and filtered while hot to remove suspended matter. The filtrate was cooled and constantly stirred, whereby a fine crystal meal was deposited. This product was filtered with suction and washed with the wash alcohol described above until the washings were practically colorless. The yield of material in this crystallization was approximately 80 g., which was considerably higher than the yield from 98% alcohol.

Physical and Chemical Data of the Abietic Acid Prepared by the New Method

Crystallographic Measurements.—Through the kindness of Dr. H. E. Merwin of the Geophysical Laboratory of the Carnegie Institution of Washington, crystallographic measurements of some crystals of abietic acid from alcohol were made and reported as follows.

"The crystals are sharply-bounded, three-sided tables with angles of approximately 45° and 90°. Most faces of 6 that were measured showed only fair or poor reflections, but identity with abietic acid as described by Graber was established with regard to habit and angles and also optical properties (as below). An unlisted form $\bar{1}01$ having small faces and giving good reflections was observed. The form m(110) was represented by small rough faces. The measurements are summarized thus: a(100)$\Lambda\mu$ ($1\bar{1}0$) = 47° 29'; a(100)Λ c(001) = 68° 22'; c(001)Λ($\bar{1}01$) = 48° 1' (calculated 48° 29'); a(100)$\Lambda\omega$($\bar{1}11$) = 70° 7'.

[9] There is good evidence that abietic acid commences to form anhydride at tem-peratures near its melting point and hence the observed melting point is not sharp.

Under the microscope, tables lying flat on (100) show the plane of the optic axes parallel to the long edge, therefore to (010); the obtuse bisectrix, γ, emerges about 15° from the center of the field; tables standing vertical, resting on the long edge, extinguish at 13° or 14°, and α is in acute angle β. The refractive indices, measured by means of the petrographic microscope with a probable error not exceeding ±0.003, are: $\alpha = 1.510$, $\beta = 1.578$, $\gamma = 1.618$. These were not previously known."

Optical Rotation Measurements.—Through the kindness of Mr. C. F. Snyder of the Sugar Laboratory, Bureau of Standards, a measurement of the optical rotatory power of a sample of abietic acid thrice crystallized from alcohol, was made in alcoholic solution. Approximately 10 g. of the acid in 100 cc. of absolute ethyl alcohol gave a reading of $[\alpha]_D^{20°} = -80.0°$. This value agrees closely with the rotation measurement of $[\alpha] -77.9°$ reported by Schulz[10] on a sample of abietic acid prepared by treating American rosin in alcoholic solution with hydrochloric acid.

Iodine Value by the Wijs Method.—The Wijs iodine number was determined upon a sample of abietic acid thrice crystallized from alcohol and dried in a vacuum. The Wijs solution was prepared as in the standard method for the determination of the iodine number of shellac. Samples weighing approximately 0.2 g., dissolved in 10 cc. of chloroform, were mixed with 25 cc. of the Wijs solution and the reaction allowed to run for one-half hour in the dark at different temperatures.

At 0° the iodine value was 153.2, 152.7; at 22–23°, 166.8, 169.3; and at 25–26°, it was 168.5, 171.1.

The theoretical iodine value for abietic acid, assuming the presence of two double bonds, is 167.9. Abietic acid appears to require very nearly two molecules of halogen for saturation.

Acid Value.—The acid number of a sample of abietic acid (melting point 161–165°) was determined by titration in alcoholic solution with standard alkali, using phenolphthalein as an indicator; 1.336 g. of material required 19.6 cc. of alkali (1 cc = 0.01265 g. of potassium hydroxide) corresponding to an acid number of 186. The theoretical acid number for a monobasic acid of formula $C_{20}H_{30}O_2$ is 185.6.

Study of Certain Metallic Abietates

Discussion of Metallic Abietates.—Manganese and cobalt resinates, made by adding a solution of a salt of one of these metals to a solution of the sodium soap of rosin, are important commercial products used as driers in paint oils and varnishes. Ellingson[11] in 1914 prepared a number of metallic derivatives of abietic acid and reported that in nearly every case the metallic abietates were acid salts. For example, he found the metal content of the manganese derivative to be 4.92%, while the normal

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[10] Schulz, *Chem. Ztg.*, **41**, 666 (1917).
[11] Ellingson, THIS JOURNAL, **36**, 325 (1914).

salt should contain 8.35%. The cobalt derivative was likewise reported to contain a very much lower percentage of metal than the theoretical content of the normal salt. On the other hand, there are commercial manganese and cobalt salts of rosin sold, with an advertised metal content in each case, which corresponds more closely to a normal salt.

A study of the abietates of lead, manganese, cobalt, nickel, iron and chromium was made, in order to settle the question whether these salts are normal, acid or basic in character.

Preparation and Analysis of Metallic Abietates

Metallic abietates were prepared from abietic acid by the following general procedure.

Freshly recrystallized acid was dissolved in about 10 times its weight of denatured alcohol and nearly neutralized by the addition of a calculated amount of strong sodium hydroxide solution of known strength. The solution was then titrated to a faint pink color with dil. alcoholic sodium hydroxide solution, using phenolphthalein as an indicator. This neutral abietate solution was then poured slowly, with stirring, into a solution of a salt of the desired metal dissolved in 40 to 50 times its weight of distilled water. A 50% excess of the metallic salt was used in order to ensure complete precipitation of the abietate. The resulting soap was thrown down as an amorphous, more or less flocculent precipitate, which was filtered on a Büchner funnel and washed thoroughly with water until free from soluble material. In cases where the product formed a gelatinous cake on the filter, it was found advantageous to transfer it to a dish and churn it with water. This mixture was then filtered again on the same funnel.

The thoroughly washed product was dried in small portions in a vacuum in order to avoid oxidation. The wet precipitate was placed in a heavy-walled test-tube and connected with an oil vacuum pump, with a drying tower of fused calcium chloride between the tube and the pump. In order to hasten the drying, the tube was placed in a water-bath at 80–90°, whereby the greater part of the moisture was rapidly removed. The last traces of water were held rather tenaciously by the metallic soap and several hours were found to be necessary for complete drying of the product.

When the metallic abietates had been partially dried, the vaporization of the remaining moisture caused the particles to fly about violently, and a wad of absorbent cotton was necessary in the mouth of the tube to prevent loss.

In case there were large aggregates of material formed, they were broken up with a spatula and the drying then continued. When the abietates were dry there was no further flying of particles observed, upon shaking the evacuated and heated tube. The dried metallic soaps were somewhat

hygroscopic and slowly absorbed oxygen from the air, especially in the case of the manganese and cobalt derivatives. For this reason the dried products were either kept in an evacuated tube or used promptly.

A description of the preparation of the individual abietates, with analyses for their metal content, follows.

Lead Abietate.—Lead abietate was prepared from sodium abietate and c. p. reagent lead nitrate. The product was pure white when fresh, but changed to a light yellow on continued exposure to air for several weeks. It was analyzed by decomposing a weighed sample in a Kjeldahl flask with sulfuric acid, using small quantities of nitric acid to oxidize organic matter. The nitric acid was subsequently removed through dilution with water and heating until the sulfuric acid reached the fuming point. The lead was determined as sulfate by the standard method.

Analyses. Calc. for $Pb(C_{20}H_{29}O_2)_2$: Pb, 25.59. Found: 24.69, 24.71.

Approximately 1.5 g. of lead abietate was ashed at low temperature in a nickel crucible, the ash extracted with distilled water and the mixture filtered. The filtrate was found to be alkaline with phenolphthalein as an indicator and when titrated hot with 0.05 N sulfuric acid, required 0.27 cc. for neutralization. This corresponded to nearly 0.5 mg. of sodium hydroxide, equivalent to 4.4 mg. of sodium abietate. It was apparent that the lead abietate contained approximately 0.25% of sodium abietate, possibly in an included form in the precipitate.

Manganese Abietate.—Manganese abietate was prepared from sodium abietate and c. p. reagent manganese sulfate. The freshly precipitated product was white with a pinkish tinge, while the material after drying was a light flesh color. It was analyzed for metal content by ashing a 0.5-g. sample in a porcelain crucible, dissolving the ash in mineral acid, and titrating the manganese by the standard bismuthate method.

Analyses. Calc. for $Mn(C_{20}H_{29}O_2)_2$: Mn, 8.35. Found: 8.17, 8.20.

Approximately 0.7 g. of manganese abietate was ashed at low temperature in a nickel crucible, the ash extracted with distilled water and the mixture filtered. The filtrate gave no color with phenolphthalein, which indicated that the manganese soap contained no appreciable amount of sodium abietate as an impurity.

Cobalt Abietate.—Cobalt abietate was prepared from sodium abietate and c. p. reagent cobalt chloride (labeled to contain only 0.18% nickel). The wet material was a deep lavender color, while the dried abietate was pale lavender, which turned to a dirty gray after an exposure of several days to the air. This change was due to oxidation: for example, approximately 0.9 g. of the product gained in weight 9 mg. during an exposure to air on the steam-bath for one hour.

Cobalt abietate was analyzed for metal content by ashing a 1-g. sample in a porcelain crucible, dissolving the ash in mineral acid and determining cobalt in the solution as metal by electrolysis.

Analyses. Calc. for $Co(C_{20}H_{29}O_2)_2$: Co, 8.91. Found: 8.44, 8.46.

Approximately 0.6 g. of cobalt abietate was ashed at low temperature in a nickel crucible, the ash extracted with distilled water and the mixture filtered. The filtrate reacted alkaline to phenolphthalein and required three drops of 0.05 normal acid for neutralization. It was evident that the cobalt abietate contained only a trace of sodium abietate as an impurity.

Nickel Abietate.—Nickel abietate was prepared from sodium abietate and c. p. reagent nickel chloride (labeled to contain a "trace" of cobalt). The dried product was light green and did not alter visibly on exposure to air. It was analyzed for metal content by decomposing a 1.5-g. sample in a Kjeldahl flask with sulfuric-nitric acid mix-

ture and precipitating nickel in the resulting solution by the glyoxime method. Another sample was ashed in a porcelain crucible, the ash dissolved in mineral acid, and the nickel determined by electrolysis.

Analyses. Calc. for $Ni(C_{20}H_{29}O_2)_2$: Ni, 8.87. Found: glyoxime method, 7.68, 7.69; by electrolysis, 7.67.

Another sample of nickel abietate was prepared from sodium abietate and c. p. nickel acetate (containing 0.07% of cobalt). Analyses was made by ashing a sample in a porcelain crucible, dissolving the ash in mineral acid and determining nickel by the glyoxime method.

Analyses. Found: Ni, 8.04, 8.13.

Approximately 0.9 g. of nickel abietate was ashed at low temperature in a nickel crucible, the ash extracted with distilled water and the mixture filtered. The filtrate was alkaline to phenolphthalein and when titrated hot with 0.05 N sulfuric acid, required 0.88 cc. for neutralization. This corresponded to nearly 1.75 mg. of sodium hydroxide, equivalent to 14.2 mg. of sodium abietate. It was evident that the nickel abietate contained approximately 1.6% of sodium abietate as an impurity.

Chromium Abietate.—Chromium abietate was prepared from sodium abietate and c. p. reagent chromium potassium sulfate. The dried product was a dirty green and was analyzed for metal content by ashing a sample in a porcelain crucible, effecting solution of the chromic oxide by a fusion method, and determining chromium by an electrometric titration.

Analyses. Calc. for $Cr(C_{20}H_{29}O_2)_3$: Cr, 5.44. Found: 1.97, 2.03.

Iron Abietate.—Iron abietate was prepared from sodium abietate and c. p. reagent ferric alum. The dried product was light brown and was analyzed for metal content by ashing a sample in a porcelain crucible, effecting solution of the ferric oxide by a fusion method, and titrating the iron by the standard permanganate method. Another sample was precipitated as hydroxide and ignited to oxide.

Analyses. Calc. for $Fe(C_{20}H_{29}O_2)_3$: Fe, 5.82. Found: 2.44, 2.59, 2.41.

Approximately 1 g. of iron abietate was ashed in a nickel crucible, the ash extracted with water and the mixture filtered. The filtrate was alkaline to phenolphthalein and required 0.55 cc. of 0.502 N acid for neutralization, corresponding to 0.011 g. of sodium hydroxide or 0.0894 g. of sodium abietate. It was evident that the iron abietate contained approximately 9% of sodium abietate as an impurity.

The conclusion was drawn that neither the iron nor the chromium abietate corresponds to a normal salt, but that they both contain an excess of abietic acid. It is well known that aqueous solutions of chromium and ferric iron are hydrolyzed and hence show an appreciable hydrogen-ion concentration. It is probable that when a neutral solution of sodium abietate is added to a chromium or iron solution, a combination of some abietate and hydrogen ions takes place with the formation of insoluble abietic acid, while a corresponding amount of metallic hydroxide forms. If this latter is in a colloidal condition, it may be subsequently removed during the washing of the precipitate. At the same time there may be the usual combination of iron or chromium ions with abietate ions to form the insoluble metallic abietates, so that the final product may be essentially a mechanical mixture of abietic acid and ferric or chromium abietate, contaminated with small amounts of sodium abietate.

The preparation of iron and chromium abietate in an organic medium was attempted in the hope that here a normal salt would result. Ferric chloride was dissolved in 95% alcohol and the solution added slowly to a neutral alcoholic solution of sodium abietate until no further precipitate was formed. The buff colored product was filtered on a Büchner funnel with suction and washed with alcohol until free from ferric chloride.

The dried product was analyzed for metal content by ashing a sample in a porcelain crucible, dissolving the ferric oxide in mineral acid, and titrating iron by the standard permanganate method.

Analyses. Calc. for $Fe(C_{20}H_{29}O_2)_3$: Fe, 5.82. Calc. for $Fe(OH)(C_{20}H_{29}O_2)_2$: Fe, 8.27. Found: 7.25, 7.23.

The product was completely soluble in cold benzene and in cold raw linseed oil, giving a deep red solution in each case. Another lot of the same material prepared in an identical manner showed on analysis an iron content of 7.69%.

The conclusion can be drawn that a basic ferric abietate of indefinite formula was formed by the interaction of ferric chloride and sodium abietate in alcoholic solution.

A solution of chromium chloride in 95% alcohol was added slowly to an alcoholic solution of sodium abietate until there was no further formation of precipitate. The product was filtered with suction, washed with alcohol and then with water, and dried in a vacuum. The bluish-green product was analyzed for metal content by ashing in a porcelain crucible, fusing the chromic oxide with sodium peroxide and titrating the chromate by the regular dichromate method.

Analyses. Calc. for $Cr(C_{20}H_{29}O_2)_3$: Cr, 5.44. Calc. for $Cr(OH)_2(C_{20}H_{29}O_2)$: Cr, 13.42. Found: 14.93, 15.16.

The product was found to be practically insoluble in benzene. The conclusion can be drawn that a basic chromium abietate, containing at least two hydroxyl groups, was formed by the interaction of chromium chloride and sodium abietate in alcoholic solution.

Discussion of Results

It was found that all of the metallic abietates described above were soluble in benzene (with the exception already noted of the basic chromium salt). This fact would indicate the absence of any appreciable amount of metallic hydroxide in the products. The metallic content found for the manganese and cobalt abietates corresponded closely to that of the normal salt. The lead and nickel derivatives were only slightly lower in metal content than required for the corresponding normal salts. The nickel abietate precipitated from nickel acetate solution was slightly higher in metal content than the material precipitated from nickel chloride solution. Possibly there may have been more hydrolysis in the case of the chloride than in the case of the acetate.

The iron and chromium abietates prepared in aqueous solution contain an excess of abietic acid. A possible reason for this has already been discussed.

The attempt to prepare normal abietates of iron and chromium by precipitation in alcoholic solution resulted in the formation of strongly basic salts of more or less indefinite composition.

Summary

1. A new method for the preparation of abietic acid from rosin is described, and physical and chemical data of the product are given.

2. Certain metallic derivatives of abietic acid are discussed and a de-

scription is given of the preparation of lead, manganese, cobalt, nickel, iron and chromium abietates from pure abietic acid.

Acknowledgment is made to Messrs. Bright, Hickson and Scherrer of the Bureau staff for their assistance in the analysis of the metallic abietates.
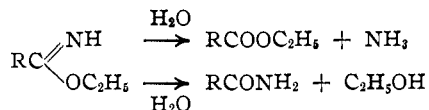
Washington, D. C.

[Contribution from the Department of Chemistry, Yale University]

THE SPONTANEOUS DECOMPOSITION OF IMIDO ESTERS

By Treat B. Johnson and Lawrence W. Bass   .

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It is well known that imido esters are extremely susceptible to hydrolytic change with formation of the corresponding oxygen esters or acid amides respectively, and that they cannot be distilled at ordinary pressure

$$RC\begin{cases} \diagup NH \xrightarrow{H_2O} RCOOC_2H_5 + NH_3 \\ \diagdown OC_2H_5 \xrightarrow[H_2O]{} RCONH_2 + C_2H_5OH \end{cases}$$

without undergoing dissociation into a nitrile and alcohol. This dissociation has also been observed to take place at ordinary temperature, and it

$$HN{=}RC{-}OCH_3 \longrightarrow RCN + CH_3OH$$

seems to be quite characteristic[1] also for the transformation to proceed beyond the nitrile stage and as a final result for the latter to undergo almost complete polymerization to its trimolecular form. In fact, Pinner[2] recommends as the best method of preparing cyaphenine $(C_6H_5CN)_3$ to allow crude undistilled benzimido-ethylether to undergo spontaneous decomposition at ordinary temperature. Wheeler, Walden and Metcalf[3] state that pure benzimido-methylether can be kept for months without change.

A most interesting and striking fact in connection with these dissociations is the pronounced tendency for the nitriles to undergo polymerization. Ordinarily these compounds, when free from impurities, are not characterized by their instability, and where polymerization has been observed it has quite generally been induced by the action of a variety of polymerizing reagents such as sulfuric acid, metallic sodium, and aluminum chloride, or by heating at high temperatures.[4]

[1] Glock, Ber., 21, 2652 (1888).

[2] Pinner, ibid., 22, 1611 (1889).

[3] Wheeler, Walden and Metcalf, Am. Chem. J., 20, 68 (1898).

[4] Pinner and Klein, Ber., 11, 764 (1878). Lottermoser, J. prakt. Chem., [2] 54, 1331 (1901). Frankland and Evans, J. Chem. Soc., 37, 563 (1880). Eitner and Krafft, Ber., 25, 2267 (1892). Scholl and Noir, ibid., 33, 1055 (1900). Meyer and Näbe, J. prakt. Chem., [2] 82, 536 (1910). Francis and Davis, J. Chem. Soc., 85, 259 (1904).