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DETECTION OF RESIN IN DRIER

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I. INTRODUCTION

In the preparation of paint by the painter a drier is added to hasten the drying. Common practice is to add about 5 parts by volume to 95 parts of oil. Commercial driers show on analysis from 2 to 10 per cent of ash, containing lead, manganese, and sometimes calcium, and from 60 to 95 per cent of volatile thinner, usually consisting of turpentine, mineral spirits,¹ or a mixture of the two. In addition to the above, what is known as "oil drier" contains linseed oil but no resin, while "japan drier" contains both linseed oil and resin.² This distinction, however, is not

¹ The term "mineral spirits" is being generally accepted for the petroleum distillates that are used as substitutes for turpentine.

² In the paint trade the resins, other than rosin, are called "gums."

strictly adhered to in the paint trade. Sometimes oil driers and japan driers are sold under other names, and there are also on the market many special and patent driers which are not used for general painting work. The resin is added to the drier to prevent precipitation of metallic soaps after thinning and to decrease the tendency of the drier to "curdle" with oil. Oil driers are made, however, containing as much as 95 per cent of mineral spirits, which contain sufficient lead and manganese to show satisfactory drying properties in laboratory tests.

The usual laboratory examination of driers includes the determination of the amount and nature of the volatile thinner, the amount and nature of the ash, a qualitative test for rosin, and drying tests with linseed oil. Purchasers of oil driers presumably desire material that is free from resins, and therefore a method for the detection of resin is needed.

II. THE SIGNIFICANCE OF RESIN IN DRIER

The following statement appears in "One Thousand More Paint Questions Answered":³

Japan driers differ from oil driers in so far as the first named are composed of gums or resins fused with linseed oil and driers such as litharge, red lead, and manganese salts. * * * Oil driers are, or should be, used for oil paints for exterior work, because, being free from resinous substances, they tend less to the cracking of paint than the excessive use of japan driers, while on the other hand, the latter should be employed where quick drying, as in flat or semiflat paints, is an absolute necessity and where surfaces are not exposed to severe weather conditions.

This statement probably expresses the ideas of those who prefer oil drier. The condemnation of "the excessive use of japan driers" is undoubtedly justified, but it is highly improbable that the small amount of resin introduced into a paint by the addition of 5 per cent of japan drier would have any bad effect for outside paints. On the contrary, Dubois⁴ showed that the addition of small amounts of "kauri mixing varnish" to linseed oil produced a vehicle that was superior to pure linseed oil for paints for iron and steel, the films being less pervious to water vapor and other gases. Toch,⁵ in a summary of the results of exposure tests of

³ Published by *The Painters' Magazine*, New York (1908).

⁴ *J. Ind. Eng. Chem.*, **5**, p. 968 (1913).

⁵ *J. Ind. Eng. Chem.*, **7**, p. 510 (1915).

painted steel plates on which different vehicles were used, includes spar varnish and a mixture of spar varnish and "stand" oil⁶ in the class which showed "a high degree of protection against corrosion." The general use of spar varnish for exterior work on metal and wood and the practice of adding spar varnish to paint vehicles indicates that the presence of resin, when the amount is not excessive, is beneficial.

In answer to an inquiry from the Bureau of Standards, several manufacturers of driers gave their opinions regarding the classification and relative values of oil drier and japan drier. All stated that while the distinction between the two as given above is technically correct it is very frequently disregarded, and that while the amount of oil drier that is made and sold is considerable it is small in comparison with the amount of japan drier that is used. Only one manufacturer claimed that oil drier is preferable to japan drier, his statement being as follows: "Except for certain purposes a high-grade oil drier is to be preferred to a kauri japan drier." The same manufacturer stated that if rosin is present in a drier, the amount should be limited. With this exception, no manufacturer stated that the presence of rosin or mineral oil has any bad effect. One manufacturer called attention to the fact that driers (called by him "resinate driers") are used, the non-volatile organic portion of which is composed entirely of resin.

Ordinarily the judicious use of japan drier will introduce from 1 to 2 per cent of resin into a paint and there appears to be no proof or general agreement among paint technologists that this small amount has any bad effect. It is improbable that its presence or absence makes any noticeable difference in painting results.

Although very good spar varnishes are made which contain small amounts of rosin, the presence of a large amount in a paint vehicle makes the latter unsuitable for outside work, and since no data are available to show the maximum amount which may be present without lowering the quality, specifications for driers and for outside varnishes almost always prohibit the use of rosin.

⁶ Linseed oil, heated and allowed to stand in tanks for three to four weeks.

III. EXPERIMENTAL

1. PREPARATION AND COLLECTION OF SAMPLES

The composition of the driers used in this investigation is shown in Table 1. The sample designated as No. 1 was prepared from linseed oil, litharge, manganese dioxide, and turpentine; No. 2 from these materials and kauri. Nos. 3, 4, and 5 were prepared from linseed oil, litharge, and manganese dioxide, no thinner being added. After all the oxides had been added to the heated oil, the mixtures were heated at 250–300° C for one-half, one, and two hours, respectively. Nos. 6, 7, and 8 were made in the same way as were Nos. 3, 4, and 5, except that red lead was substituted for litharge and the samples were thinned with turpentine. Seven more samples, Nos. 9 to 15, inclusive, were prepared from various resins and oils, manganese dioxide, litharge, and turpentine, the mixtures of oil, resin, and oxides being heated for one hour at 250–300° C. Nos. 16 to 39, inclusive, were obtained from manufacturers⁷, the data regarding the composition of these samples being compiled from the statements of the makers. In the preparation of commercial driers, the mixtures of oil, resin, and metallic compounds are heated for so long a time and at so high a temperature that the percentages of oil and of resin in the finished driers can be only approximately estimated.

2. PRELIMINARY EXPERIMENTS

Rosin can be detected, of course, by the well-known Liebermann and Storch test with acetic anhydride and sulphuric acid. Attempts to identify and detect other resins by the color test of Hicks⁸ were not successful. Determination of the acid number of the mixtures of unsaponifiable matter, fatty acids, and resin acids, obtained from the driers by saponification and subsequent treatment with acid, was found to be useless as a means for the detection of resin, because prolonged heating during the preparation of oil drier lowered the acid number very much. For

⁷ For samples and information the author is indebted to the following: John Lucas & Co. (Inc.); W. P. Fuller & Co.; Samuel H. French & Co.; Pitcairn Varnish Co.; Pratt & Lambert; Sherwin-Williams Co.; and the O'Brien Varnish Co.

⁸ *J. Ind. Eng. Chem.*, **3**, p. 86 (1911).

instance, the mixtures of unsaponifiable matter and fatty acids obtained from Nos. 3 and 5 (heated for one-half and two hours, respectively) showed acid numbers of 186 and 165, respectively.

3. DETECTION OF RESIN BY THE ALCOHOL METHOD

The mixtures of unsaponifiable matter, resin acids, and fatty acids, obtained from the driers as stated above, were treated with ethyl alcohol of two strengths, 95 and 97 per cent by volume. In most cases the samples containing resins other than rosin showed a marked turbidity or a deposit of insoluble matter. It will be noted from the results of these tests, as shown in Table 1, that to obtain clear solutions with Nos. 6 to 8, inclusive, it was necessary to use 97 per cent alcohol. With these samples the use of 96 per cent alcohol gave solutions that were very faintly turbid. It will be noted also that by this method it was impossible to detect the presence of rosin, manila, shellac, and the very small amounts of kauri that were present in Nos. 34 to 36, inclusive.

4. DETECTION OF RESIN BY ESTERIFICATION AND SUBSEQUENT DETERMINATION OF THE ACID NUMBER

The usual method for the determination of oil and resin in mixtures of the two includes esterification by Twitchell's⁹ method, using absolute alcohol and dry hydrochloric-acid gas, or by Wolff's¹⁰ method, using absolute alcohol and concentrated sulphuric acid. Preliminary experiments with fatty acids prepared from linseed oil, the results of which are shown in Table 2, showed that more nearly complete esterification was obtained by the former method, absolute ethyl alcohol being used. As is also shown in Table 2, variation of from two to five minutes in the time of heating in the Wolff method did not affect the results obtained with the mixtures of acids and unsaponifiable matter from oil drier and japan drier. The Wolff method is shorter and simpler than the Twitchell method, and the results obtained with various samples of driers, as given in Table 3, show that as a qualitative test for resin the former is satisfactory. The maximum figure for acid number after esterification was 9 for oil driers and the minimum figure for japan driers was 11. Since the figure obtained with

⁹ J. Soc. Chem. Ind., 10, p. 804 (1891).

¹⁰ Chem. Ztg., 38, pp. 369-370, 382-383, 430 (1914).

No. 34 is within experimental error of the maximum figure for oil drier, the method can not be depended upon to detect less than 6 per cent of resin in the ash-free nonvolatile portion of a drier. This is ordinarily equivalent to a resin content of less than 3 per cent in a thinned drier ready for use. The figures obtained with driers are given as whole numbers because the end point of the titration, using phenolphthalein as indicator, was so obscured as to cause a possible error of 0.1 cc of 0.25 N alkali. This would result in an error of 1.4 in the acid number determined with a 1 g sample. In fact, an accuracy of two in the determination of acid number is all that can be expected. Samples that weigh over 1 g can not be used since the solutions would then be too dark in color.

TABLE 1
Detection of Resin by Alcohol Method

No.	Constituents other than thinner and metallic oxides		Name of drier given by manufacturer	Appearance of alcohol solution	
	Per cent of oil	Per cent of resin		95 per cent alcohol	97 per cent alcohol
1	Linseed, 48	None		Clear	
2	Linseed, 38	Kauri, 8		Turbid	Turbid.
3	Linseed, 85	None		Clear	
4	do	do		do	
5	do	do		do	
6	Linseed, 45	do		Turbid	Clear.
7	Linseed, 47	do		do	Do.
8	Linseed, 48	do		do	Do.
9	Linseed, 25; Chinese wood, 12	do		Clear	
10	Linseed, 26	Kauri, 6		Turbid	Turbid.
11	do	Manila, 5		Clear	Clear.
12	Linseed, 28	Manila, 8		do	Do.
13	Linseed, 30	Dammar, 6		Turbid	Turbid.
14	Linseed, 27	Rosin, 7		Clear	
15	Linseed, 25	Shellac, 5		do	
16	Linseed	Rosin	Japan	do	
17	do	None	Oil	do	
18	do	do	do	do	
19	do	"Copal gum"	Gum	Turbid	Do.
20	do	Rosin	Resin	Clear	
21	Linseed, 50	None	Specification	do	
22	Linseed, 12	Kauri, 10		Turbid	Do.
23	Linseed, 27	Rosin, 7	High-grade commercial.	Clear	
24	Linseed	"Vegetable gum."	Coach painters' japan.	Turbid	Do.

TABLE 1—Continued
 Detection of Resin by Alcohol Method—Continued

No.	Constituents other than thinner and metallic oxides		Name of drier given by manufacturer	Appearance of alcohol solution	
	Per cent of oil	Per cent of resin		95 per cent alcohol	97 per cent alcohol
25	Linseed	None	Standard japan...	Clear	
26	Linseed, 18	"Fossil gum," 14.	Japan	Turbid....	Slightly turbid.
27	Linseed, 22	None	Oil.....	Clear	
28	Linseed	do	do	do	
29	do	Kauri	Japan	Turbid....	Turbid.
30	do	Kauri, Rosin	do	do	Do.
31	do	Rosin	do	Clear	
32	do	do	do	do	
33	do	do	do	do	
34	Linseed, 25	Kauri dust, 1½.	do	do	
35	Linseed, 28	Kauri dust, 1	do	do	
36	Linseed, 26	Kauri dust, 1½.	do	do	
37	None	Rosin	Resinate	do	
38	Linseed	None	Linoleate	do	
39	do	do	do	do	

TABLE 2
 Results with Twitchell and Wolff Methods of Esterification

Material	Method	Time of heating	Acid number (mg. of KOH per gram of acids + unsaponifiable matter)
Fatty acids + unsaponifiable matter from raw linseed oil	Twitchell	Minutes	{ 2.7 3.3
		Average	
		Fatty acids + unsaponifiable matter from raw linseed oil	Wolff
Average			6.2
Fatty acids + unsaponifiable matter from oil drier, No. 8....	Wolff	2	8
		3	8
		5	7
Fatty acids + resin acids + unsaponifiable matter from japan drier, No. 12.....	Wolff	2	19
		3	18
		5	19

TABLE 3

Results with Driers, using Wolff Method of Esterification

Sample	Acid Number	Average.
Oil drier No. 6; linseed oil, 45 per cent.....	{ 9 7 }	8
Oil drier No. 7; linseed oil, 47 per cent.....	{ 8 8 }	
Oil drier No. 8; linseed oil, 48 per cent.....	{ 7 7 }	7
Oil drier No. 8a ^a	{ 9 7 }	
Oil drier No. 27; linseed oil, 22 per cent.....	{ 9 8 }	8½
Japan drier No. 10 { linseed oil, 25 per cent..... {kauri, 6 per cent.....	{ 13 13 }	
Japan drier No. 11 { linseed oil, 26 per cent..... {manila, 5 per cent.....	{ 14 16 }	15
Japan drier No. 12 { linseed oil, 28 per cent..... {manila, 8 per cent.....	{ 19 18 }	
Japan drier No. 15 { linseed oil, 25 per cent..... {shellac, 5 per cent.....	{ 16 16 }	16
Japan drier No. 34 { linseed oil, 25 per cent..... {kauri dust, 1½ per cent.....	{ 11 11 }	
Japan drier No. 35 { linseed oil, 28 per cent..... {kauri dust, 1 per cent.....	{ 13 15 }	14
Japan drier No. 36 { linseed oil, 26 per cent..... {kauri dust, 1½ per cent.....	{ 12 14 }	

^a No. 8 without thinner.

IV. PROPOSED METHOD FOR THE DETECTION OF RESIN IN DRIERS

(1) Test for rosin by the Liebermann and Storch method with acetic anhydride and sulphuric acid.

(2) If no rosin is detected by (1), place about 25 cc of the drier in a flask and pass in a rapid current of steam while heating the flask in an oil bath at 130° C. Add an excess of alcoholic potash, and heat on the steam bath for one hour. Add an excess of hydrochloric acid and shake vigorously. Fill the flask with hot water and allow the oily layer to collect in the neck of the flask. Remove about 5 cc of this oily layer to another flask, add about 25 cc of dilute hydrochloric acid (1:1), and boil for a few minutes. This is necessary to insure the decomposition of all metallic soaps.

Cool, add about 20 cc of ether and sufficient water to bring the ether solution into the neck of the flask. Filter a portion of this ether solution into a flask, evaporate off the ether, and dry the residue at 110–115° C for one-half hour. Place 0.15–0.20 g of this residue in a test tube, add 5 cc of ethyl alcohol (97 per cent by volume), and shake. A turbidity or a deposit of insoluble matter shows the presence of resin in the sample.

(3) If no resin is detected by (1) or (2), filter into a tared flask a sufficient amount of the ether solution obtained in (2) to yield a dry residue of 0.8–1.0 g. Evaporate and dry as stated under (2) and weigh the flask and dried residue. Add 10 cc of absolute ethyl alcohol, warm gently till the solution is clear, and add a mixture of 10 cc of absolute ethyl alcohol and 3 cc of concentrated sulphuric acid. Boil under a reflux condenser for two or three minutes, cool, and transfer the contents of the flask to a separatory funnel, washing out the flask with water and ether. Add 25 cc of a 10 per cent solution of sodium chloride and shake. Draw off the lower layer and shake it with 50 cc of ether. Unite the ether solutions and wash with water until the washings are neutral. Three washings will usually suffice. Transfer the ether solution to a large flask and dilute with neutral 95 per cent alcohol until the color of the solution is sufficiently light to permit of titration with 0.25 N alcoholic potash, using phenolphthalein as indicator. Dilution to 400–600 cc is generally necessary. If the dilution with alcohol causes a turbidity, add sufficient ether to clear the solution. Titrate with 0.25 N alcoholic KOH and calculate the acid number as milligrams of KOH per gram of the mixture of unsaponifiable matter and acids taken. An acid number of over 10 shows the presence of resin in the sample.

V. SUMMARY

A method has been developed for the detection of resin in driers which is reliable except when the resin content is very small, e. g., less than 6 per cent of the ash-free nonvolatile portion.

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