

STUDIES IN THE PREPARATION OF OXIDATION-RESISTANT MODIFIED ROSINS

Part I.—Use of Sulphur for the Modification of Rosin and its Esters

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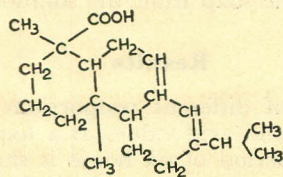
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A study of the rosin-sulphur reaction with a view to reducing the oxidation properties of rosin has been carried out. It has been found that the treatment of rosin with sulphur (5%) at 240–50°C. for one hour reduces the oxidation properties of rosin and its esters to negligible proportions. Data of the physical properties and oxygen absorption of the sulphur-treated resins and the methods of treatment are presented in this paper.

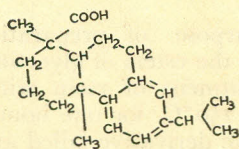
Introduction

Rosin is composed of 90% resin acids and 10% non-acidic materials. The resin acids are a mixture of isomers of alkylated hydroaromatic derivatives of 1-methyl-7-isopropylphenanthrene and the structure of the more stable abietic acid is given below.



Abietic acid

The two double bonds in the abietic acid molecule represent a degree of unsaturation which makes the compounds highly unstable. The accepted shortcomings of rosin itself for coating compositions can be attributed for most part to oxidation at the double bonds. In particular, the discoloration and embrittlement characteristics are clearly bound up with its tendency to oxidise. The glaring disadvantages of instability have long been recognised and numerous attempts, which have been made to overcome this draw-back, are discussed below.



Dehydroabietic acid

Polymerisation.—Oxidation is greatly reduced because of the conversion of a large part of rosin

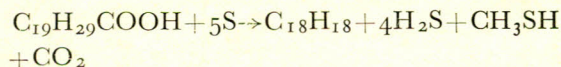
to a heterogenous dimer. The molecular weight of rosin is increased by about 70% and the polymerised materials have increased melting point, are commercially produced¹ and find wide use in the preparation of improved coating compositions.

Hydrogenation.—The use of nickel² or copper chromite³ as catalyst reduces the melting point of rosin, and therefore the hydrogenated product can be used only in adhesives and rubber industries. The use of catalysts such as Pd, Rh and Ru, however, at 125–300°C. under a pressure of about 3,000 p.s.i.⁴ or hydrogenation⁵ of polymerised rosin and subsequent esterification give products having a melting point in the range of 75–85°C.

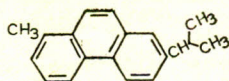
Oxidation.—Ozonised air has been suggested for oxidation. It gives a dark coloured product having a higher melting point. The oxidised rosin, though soluble in alcohol, ketones, etc. is insoluble in petroleum solvents and this limits its application in coating compositions.

Conversion to Dehydroabietic Acid.—This acid can be prepared by the oxidation of abietic acid with selenium dioxide, followed by dehydration by boiling with acetic acid. Potassium permanganate and bromine have no effect on it. Heat treatment brings about partial conversion of rosin to the more stable dehydroabietic acid, but the temperature proposed for this treatment tends to substantially decarboxylate the molecule. The use of iodine as catalyst has been proposed to effect this conversion at a lower temperature in order to reduce the decarboxylation, but the simplest and probably the most promising way is the treatment with sulphur and this work is mostly covered by patent literature.^{6–9}

Diels and Karstens¹⁰ have shown that abietic acid reacts with sulphur as follows:



Retene ($C_{18}H_{18}$) has the following structure.



Retene

However, it is claimed that under appropriate conditions, the action of sulphur leads to the formation of dehydroabietic acid. The improvements effected by any of the other methods is either limited or requires expensive catalysts as well as complicated and delicate treatment procedures, and it was therefore considered desirable to investigate the rosin-sulphur reaction for reducing the oxidation properties of rosin. The present investigations may be divided into two parts: (1) Studies on the influence of different proportions of sulphur at varying temperatures on melting point, acid value, unsaturation and film forming properties of rosin, and (2) Studies of the oxidation properties of some of the selected modified rosins and their esters.

Experimental

Apparatus.—All the reactions were carried out in a three-necked flask, with arrangement for stirring, a carbon dioxide inlet to provide inert atmosphere and a distillation connection to remove the water of reaction.

Treatment of Rosin with Sulphur.—Rosin was added to the flask, the apparatus assembled and the air flushed out with carbon dioxide. The flask was heated to the desired temperature in a mantle regulated by a variac and sulphur was added gradually in a total time of about 15 minutes. Progress of the reaction was noted by taking samples periodically and examining for melting point, acid value and iodine value. Control batches without the incorporation of sulphur were also run to evaluate the extent of decarboxylation.

Preparation of the Derivatives of Sulphur-treated Rosin.—Calcium derivative was prepared by adding slaked lime to the treated material and heating at 240°–250°C. till there was no further reduction in acid value. The glycerol and pentaerythritol esters were prepared by adding the calculated molar quantities in instalments at 270°–280°C.

Methods Used for Testing Resins.—The acid value was determined by dissolving about 1 g. sample of the resin in 15–20 ml. of xylene and titrating to a phenolphthalein end point with alcoholic 0.1 N sodium hydroxide. The iodine value was determined by the Hanus method using about 0.1 g. of the sample, melting point by capillary method and scratch hardness by the standard scratch testing apparatus.

Stability Tests for Modified Products.—(1) A 2g. sample of the powdered material was collected on a petri dish, kept in a stream of oxygen for 15 days and the weight increase recorded at regular intervals. Control tests were performed upon untreated rosin and its derivative. (2) A 10% solution of the sodium soaps of untreated and treated rosins was prepared and the extent of oxidation was evaluated by the amount of precipitation of the soap from the solution.

Results

The effect of different proportions of sulphur on the iodine and acid values at a temperature of 280°C. for a period of six hours is shown in Fig. 1. The iodine value curves show that maximum reduction in unsaturation takes place during the first two hours and the acid value curve shows that the reduction in acidity is due mainly to decarboxylation. The influence of reaction temperature on the reaction products for a two-hour heating period was studied and is shown in Fig. 2. These data show that the best results are obtained at 250°C. with a minimum of decarboxylation. It was also found that melting point of rosin was lowered by 4°C. with 5% S and 8°C. with 7.5% S. The use of 7.5% sulphur also affects the film-forming properties of rosin, as the reaction products give a tacky film. The scratch values remain unaffected.

For the purpose of preparation of calcium derivative and the esters of glycerol and pentaerythritol, pretreatment of rosin with sulphur was carried out at 250°C. for one hour. Attempts to prepare the zinc derivative failed and the addition of even 0.5% gave an opaque product. This is in contrast with the behaviour of the unmodified rosin. The details of formulations and properties of the various derivatives prepared are presented in

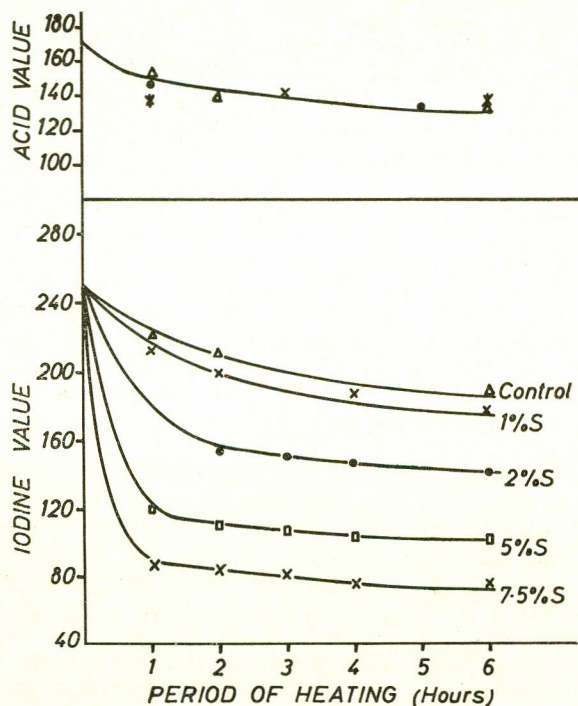


Fig. 1.—Influence of duration of heat and different proportions of sulphur on iodine and acid value of treated rosin.

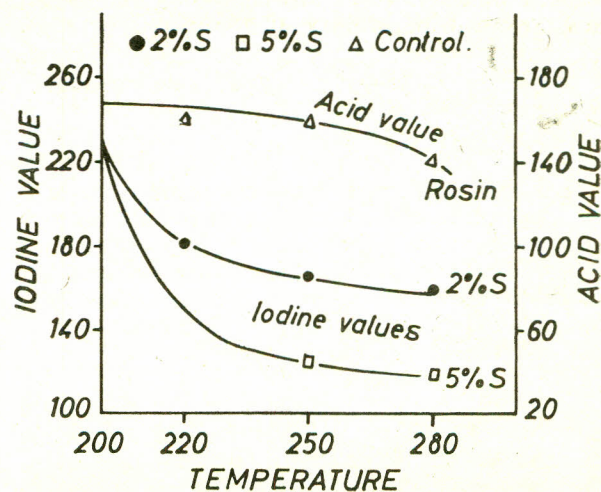


Fig. 2.—Influence of reaction temperature on iodine and acid values of treated rosin.

Table 1. The colour of these products was lighter than of those prepared from unmodified rosin.

The oxidation studies were carried out on resin nos. 3 and 5, unmodified rosin and ester gum (prepared from unmodified rosin). The data is presented in Table 2. The results show that 5%

TABLE I.—FORMULATIONS AND PROPERTIES OF MODIFIED ROSINS.

No.	Constituents				Properties			
	S. %	Ca(OH) ₂ %	Glycerol %	Pentaerythritol %	Melting point °C.	Iodine value	Acid value	Scratch hardness (g.)
1.	2.0	2.0	—	—	88–92	149	113.8	150
2.	2.0	5.0	—	—	130–32	160	56	200
3.	5.0	5.0	—	—	130–60	111	70	125
4.	5.0	5.0	5.0	—	120–50	110	34	150
5.	5.0	0.5	12.5	—	74–88	104	12.8	—
6.	5.0	0.5	—	10	95–105	101	35.0	250

TABLE 2.—OXYGEN ABSORPTION OF RESINS.

Resin	% total increase in weight of sample after							
	1 day	2 days	3 days	5 days	6 days	7 days	15 days	
No. 3	..	0.10	0.16	0.27	0.34	0.38	0.40	0.60
No. 5	..	0.17	0.25	0.26	0.36	0.40	—	—
Resin	..	2.8	4.1	4.4	6.6	7.2	7.6	9.1
Ester gum	..	—	4.0	4.5	6.3	7.0	7.5	9.5

sulphur treated rosin is resistant to oxidation and compares well with the results reported for commercial polymerised rosins. Seven-day oxygen absorption for Dymex, polypale and unmodified rosin is reported as 0.15, 0.55 and 9.17% respectively. These results were further confirmed by studying the stability of sodium soap solutions. It was found that there was a slight precipitation in the soap solution of unmodified rosin after twenty-four hours and this increased to about 41.0% of the total dissolved solids after five months. On the other hand, the solution of soap made from rosin treated with 5% sulphur remained clear at the end of this period.

It appears from the present studies that there is no need to reduce the unsaturation completely in order to obtain oxidation-resistant properties. It is probable that dehydroabietic acid acts as an anti-oxidant and helps in imparting this exceptional degree of stability achieved by the sulphur-treated rosin. However, this aspect needs further investigation.

Conclusions

Treatment of rosin with sulphur (5%) at 240-250°C. for one hour reduces the oxidation properties of rosin and its esters to negligible proportions and in this respect it compares favourably

with polymerised rosin and is much better than maleic modified rosin. The film-forming properties of the esters of these sulphur-treated rosins are, however, somewhat inferior to the above mentioned products but are comparable with those prepared from unmodified rosin. The use of sulphur treatment for rosin therefore, if adopted by our industry, will help in the production of improved qualities of oleo-resinous varnishes.

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