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STUDIES IN THE PREPARATION OF OXIDATION-RESISTANT MODIFIED ROSINS

Part II. Preparation and Properties of Stable Fused and Precipitated Cobalt Rosinates

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Abstract. Cobalt derivatives of oxidation-resistant sulphur-modified rosins by fusion and precipitation methods have been prepared. Fused rosinates do not block and varying amounts of cobalt have been incorporated successfully up to a maximum of equivalent combining ratio. The improvement in properties, i.e. stability, Co content, solubility and rate of drying, have been studied in this paper.

The treatment of rosin with sulphur under appropriate conditions reduces the oxidation properties of rosin and its esters to negligible proportions.[1] In this respect, it was shown to be comparable with other modified rosins, i.e. polymerized, maleic modified. The advantages achieved in sulphur-modified rosin are carried through when used in the preparation of metallic rosinates. Present studies are limited to the preparation and properties of cobalt rosinate from sulphur-modified rosin.

The production of cobalt rosinate is an important process in the preparation of 'driers' widely used in surface coating and printing ink industries. The usefulness of a rosinate depends on its solubility in oils and solvents, high metal content and resistance to oxidation. Cobalt rosinates are generally prepared by (1) precipitation process (2) fusion process. Precipitation process consists in double decomposition between a water-soluble salt of rosin and a water-soluble salt of cobalt. Precipitated rosinate contains approximately stoichiometric amount of cobalt (7.5–8%). It is a finely divided compound of an active metal and an oxidizable anion which results both in poor storage quality and solution stability. In fusion process, it is prepared by direct fusion of rosin and an active cobalt compound. This is comparatively simple; the quality of the product is better in respect of solubility in organic solvents and can be stored more easily than precipitated rosinates. Fused rosinates have low cobalt content owing to the tendency to block at reaction temperature when the metal exceeds 3.5%. However, the blocking difficulties were overcome and theoretical amount of cobalt were incorporated in modified rosins using special technics.[2] Hydrogenated[3] and polymerized[4] rosins have been reported to form cobalt rosinates with 18% and 19% of metal respectively but this does not increase cobalt content available as drier. Similar results have also been reported[5] by the use of rosin whose optical rotation has reached in the range of 30–50° in the solid state by heating in the range of 250–350°C. Clair *et al.*[6] used a variety of aldehydes to modify rosin for the preparation of metal rosinates containing stoichiometric quantity of metal.

The improvement effected by any of these methods involves modification of rosin by treatment under delicate experimental conditions. These can be carried out successfully in the laboratory but are quite difficult to do so industrially. It has been found that the fusion of sulphur-modified rosin and an active cobalt compound provides a simple course for the preparation of cobalt rosinates. The blocking difficulties are completely overcome and varying quantities of cobalt can be incorporated up to a maximum of equivalent combining ratio. Also, the fused and precipitated products based on sulphur-modified rosins have improved oxidation-resistant properties.

Experimental

Sulphur-modified rosin used in the preparation of cobalt rosinates was prepared by treating rosin with sulphur (5%) in the temperature range of 240–50°C for 1 hr. Characteristics: acid value, 148; sap. value, 158; iodine value (Hanus method), 120; softening point, 80°C.

Fusion Process. Sulphur-modified rosin was heated in a four-necked round-bottomed flask fitted with a thermometer, stirrer and a distillation connection to remove water of reaction. The charge was heated to 170°C and cobalt acetate tetrahydrate was added in parts allowing sufficient time to react before other portion was added. When the full quantity had been added, the temperature was maintained for 1 hr. The temperature was then slowly raised to 220±5°C and heated further over a period of 20–90 min depending upon the quantity of cobalt acetate added. The mass was kept stirred throughout and excessive heating was avoided. At the end, the temperature was raised to 250°C to facilitate pouring out the product. Oxides and carbonates of cobalt required higher temperatures and longer reaction time.

Precipitation Process. Precipitated cobalt rosinate was prepared by double decomposition between sodium soap of sulphur-modified rosin and a water-soluble salt of cobalt. Sodium soap solution (10%) was formed by adding powdered modified rosin to boiling aqueous solution of caustic soda and was further kept at boil for 1 hr. Slightly less than the stoichiometric amount of alkali was taken to keep the solution on acid side. The rosinate was precipitated by the slow addition of aqueous solution (10%) of a cobalt compound while the whole mass was kept

agitated. The precipitate was filtered, washed several times with water and finally dried in vacuum at 50°C.

Properties

Fused cobalt rosinates prepared from modified rosin were blue homogeneous amorphous resin-like solids while the precipitated products were finely divided grey powders.

Cobalt Content. Varying quantities of cobalt were incorporated in fused rosinates up to a maximum corresponding to free carboxyl groups as shown in Table 1. Rosin oil prepared by distillation of sulphur-modified rosin reacted with approximately double the quantity of cobalt acetate required theoretically due to the formation of a mixed acetate–abietate. Cobalt content in precipitated rosinate from modified rosin was, however, slightly less than in the precipitated product from unmodified rosin.

Solubility. Sulphur-modified fused and precipitated cobalt rosinates were soluble in turpentine, kerosene, drying oils, benzene, toluene, xylene and chloroform in concentration up to 40–50% solid. Solutions in mineral turpentine precipitated on standing to form gels if the concentration exceeded 12% solid. Cobalt derivatives of rosin oil (from modified rosin) were exceedingly soluble in all common paint and varnish solvents.

Stability. Solutions of modified fused and precipitated cobalt rosinates in gum turpentine and mineral turpentine containing 0.5–3.5% and 0.75% Co respectively were prepared and examined periodically. The solutions remained stable after a period of one year. There was, however, slight increase in viscosity with time in stronger solutions. The stability was further confirmed by placing 0.2 g of powdered samples (passing 120 mesh) in a petri dish (dia 5.5 cm) and were exposed to oxygen. Fused and precipitated cobalt rosinate prepared from sulphur-modified rosin showed 2.0% and 1.8% increase in weight respectively whereas the precipitated product prepared from unmodified rosin gained 5.5% in weight after 15 days.

Rate of Drying. The quality of fused sulphur-modified cobalt rosinate was tested by incorporating with raw linseed oil in varying proportions and was compared with cobalt naphthenate under identical conditions. The drying period was determined by applying a film on glass plates (6×2 in) and the oil was allowed to drain by inclining the plates at an angle of approximately 45° for 15 minutes. The plates were then placed in horizontal position and the central portion was tested for touch dry period. The results are given in Table 2.

TABLE 1. COBALT ROSINATES PREPARED FROM SULPHUR-MODIFIED ROSIN AND ROSIN OIL.

Sulphur-modified rosin (parts by wt)	Rosin oil * (parts by wt)	Cobalt acetate (parts by wt)	Stoichiometric amount of cobalt acetate (parts by wt)	Co in finished product (%)	Softening point (ring and ball) °C
100	—	20	32·9	4·2	123
100	—	30	32·9	6·4	132
100	—	34	32·9	7·0	154
100	—	40	32·9	8·5	157
—	100	25	13·4	5·3	Paste
—	100	30	13·4	6·1	Thick paste
—	100	41	13·4	6·8	Thick paste

*Rosin oil (acid value, 60) was prepared by distillation of sulphur-modified rosin.

TABLE 2. COMPARISON OF DRYING RATES OF RAW LINSEED OIL CATALYSED WITH FUSED SULPHUR-MODIFIED COBALT ROSINATE AND COBALT NAPHTHENATE..

Cobalt (%)		Time for film to touch dry	
Sulphur-modified rosinate drier	Naphthenate drier	hr	min
0·02	—	6	30
—	0·02	6	45
0·04	—	5	—
—	0·04	4	45
0·06	—	4	—
—	0·06	4	—
0·08	—	3	30
—	0·08	3	45
0·10	—	3	15
—	0·10	3	15

Conclusions

Stable fused and precipitated cobalt rosinates containing stoichiometric amounts of metal can be prepared by the use of sulphur-modified rosin. The blocking tendencies of fused rosinate are eliminated. The products have good solubility and improved stability to oxidation over unmodified rosin.

References

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