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STUDIES IN THE PREPARATION OF OXIDATION—RESISTANT MODIFIED ROSINS

Part III. Preparation and Properties of Stable Fused and Precipitated Zinc Rosinates

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Abstract. Stable fused zinc derivatives of oxidation-resistant sulphur-modified rosins containing varying amounts of zinc have been prepared without blocking difficulties. Reaction conditions and improvement in properties over unmodified rosins are described in this paper.

Zinc rosinate is an important product which is extensively used in printing inks and surface coating formulations due to its properties of low reactivity with drying oils, compatibility with alkyds and ethyl cellulose, improved gloss, dispersing action and inertness to basic pigments. Commercially, zinc rosinate is prepared by precipitation and fusion processes, the former involves double decomposition between a water-soluble soap of rosin and a zinc salt while the latter is the result of direct fusion of rosin and an active zinc compound. Metal rosinates are generally assessed by their solubility in oils and common paint and varnish solvents, high metal concentration and resistance to oxidation. Precipitated zinc rosinate contains a stoichiometric quantity of metal (8.5–9.0%) but suffers both from poor solubility and storage quality. Fused zinc rosinates, on the other hand, have good solubility properties but have the disadvantage of a low metal content compared with precipitated product. This is due to the tendency to 'block' (partial crystallization of zinc abietate causing opaqueness and infusibility of the mass) during reaction when a small fraction of theoretical requirement of a zinc compound is incorporated at reaction temperature. Numerous attempts have been reported[1–6] to overcome this difficulty. However, most of them can be carried out successfully in the laboratory but are quite difficult from commercial point of view.

On the basis of the work conducted in these Laboratories, the reaction of rosin with sulphur under appropriate conditions resulted in an oxidation-resistant product[7] which eliminated most of the blocking difficulties frequently observed in the preparation of metallic rosinates. Studies in the preparation and properties of cobalt derivatives prepared from oxidation-resistant sulphur-modified rosins have been reported in previous communication.[8] The present work is limited to the preparation of precipitated and fused zinc rosinates prepared from sulphur-modified rosins. Various zinc compound swere fused satisfactorily with sulphur-modified rosins with a metal concentration corresponding to the free carboxyl groups. However, double the theoretical requirement of metal was incorporated when zinc acetate was used giving a mixed acetate-abietate. Rosin oil and rosin esters of low acid value, prepared from sulphur-modified rosins, reacted with many times the expected quantity of zinc acetate that can be accounted for by the formation of either a zinc diabietate or zinc acetate-abietate.

Experimental

Sulphur-modified rosins used in the preparation of zinc rosinates were prepared by treating rosin with varying proportions of sulphur in the temperature range of 240–50°C for 1 hr. Characteristics of these modified rosins are given in Table 1.

Fusion Process. Sulphur-modified rosin was heated in a four-necked round-bottomed flask fitted with a thermometer, stirrer, inlet for CO_2 and a distillation connection. The charge was heated to an appropriate temperature and the zinc compound was added in parts over a period of 15–30 min to avoid excessive frothing. When the full quantities had been added, the temperature was maintained for 0.5–2.0 hr depending upon the nature of the zinc compound used. Excessive heating was avoided and the mass was kept stirred throughout. The temperature was finally raised by 30°C to increase the mobility of the product. The acetate, carbonate and hydroxide of zinc were fused directly. The reaction was catalysed with acetic acid when zinc oxide was used. Reaction conditions and properties of various zinc rosinates prepared from sulphur-modified rosins are given in Table 2.

Precipitation Process. The sodium soap of sulphur-modified rosin was prepared by saponification with slightly less than theoretical amount of caustic soda to keep the solution acidic. Zinc rosinate was precipitated by the slow addition of aqueous solution (10%)

TABLE 1. CHARACTERISTICS OF SULPHUR-MODIFIED ROSINS.

Parts of sulphur/ 100 parts of rosin	Acid value	Saponification value	Iodine value (Hanus)	Softening point (ring and ball)°C
2.5	155	160	157	76
5.0	152	156	119	74
7.5	142	149	85	72
—	165*	171*	250*	78*

*Unmodified rosin.

of a zinc salt to the sodium soap solution (10%) while the whole mass was kept agitated. The precipitate was filtered, washed several times with water aud dried *in vacuo* at 50°C.

Properties

Fused zinc rosinates prepared from sulphur-modified rosins were clear homogeneous amber-coloured solids. The colour varied with the reaction conditions, type of zinc compound and the colour of the modified rosin used. Comparatively light coloured products were formed when the reaction was carried out in an inert atmosphere. Precipitated zinc rosinates were ivory-white finely divided powders.

Zinc Content. Theoretical and maximum zinc content of zinc rosinates are compared in Table 2. When zinc acetate was fused, the maximum metal concentration obtained was double the theoretical amount forming mixed acetate-abietate. In contrast, rosin oil, ester gum and pentaerythritol ester of low acid value prepared from sulphur-modified rosin reacted in proportions approximately 8–32 times the zinc acetate required for the formation of neutral diabietate. Zinc carbonate fused with rosin modified with 2.5% sulphur blocked the product when the quantity of metal compound exceeded 12 parts per 100 parts of modified rosin against 17.3 parts required theoretically. The blocking difficulty was overcome when zinc carbonate was fused with rosin modified with 5% sulphur and stoichiometric quantity of zinc was incorporated Zince hydroxide, however, followed normal course of reaction with rosins modified with varying proportions of sulphur. Zinc content in precipitated rosinates prepared from sulphur modified rosins was slightly less than in the precipitated product from unmodified rosin.

Softening and Melting Points. Softening points of fused rosinates were determined by ring and ball method. The softening point depended upon the amount of zinc, type of modified rosin and the zinc compound used. Rosinates containing equivalent amounts of metal prepared from different metal compounds showed a variation of 8–16°C. Melting points of precipitated rosinates, determined by capillary method, were not sharp and showed a drop of 20–25°C as compared with precipitated product from unmodified rosin.

Solubility and Stability. All the fused zinc rosinates were soluble in benzene, toluene, turpentine, mineral spirit, kerosene, naphtha, acetone and ethyl acetate in concentrations up to 30–70% solid. Solutions of modified rosinates with stoichiometric metal content prepared in turpentine and mineral spirit in concentrations in the range of 25–40% solid remained clear after standing over a period of 2 months. Solutions of rosinates prepared from rosin treated with sulphur (7.5%) showed exceptionally good solubility and stability with a metal concentration approaching twice that in the diabietate. Solutions of precipitated

TABLE 2 FUSED ZINC ROSINATES PREPARED FROM SULPHUR-MODIFIED ROSINS AND THEIR DERIVATIVES.

Zinc compound	Sulphur-modified rosin (parts by wt)			5% Sulphur-modified rosin derivative (parts by wt)			Acid value	Stoichiometric amount of zinc compound (parts by wt)	Amount of zinc compound reacted (parts by wt)	Reaction temperature (°C)	Reaction time (hr)	Softening point (ring and ball) (°C)
	2.5%	5.0%	7.5%	rosin oil	ester gum	Pentaerythritol ester						
Zinc acetate	100	—	—	—	—	—	155	30·3	30·3	220±5	1·0	132
(dihydrate)	100	—	—	—	—	—	155	30·3	60·6	260±5	0·5	145
$(CH_3COO)_2$ Zn. $2H_2O$	—	100	—	—	—	—	152	29·7	29·7	220±5	1·0	131
	—	100	—	—	—	—	152	29·7	59·4	260±5	0·5	143
	—	—	100	—	—	—	142	27·8	27·8	220±5	1·0	125
	—	—	100	—	—	—	142	27·8	55·6	260±5	0·5	142
	—	—	—	100	—	—	60	11·7	90·0	220±5	2·0	Thick Paste
	—	—	—	—	100	—	18	3·5	111·0	260±5	1·5	122
	—	—	—	—	—	100	22	4·3	109·9	260±5	1·5	124
(ZnO)	—	100	—	—	—	—	152	11·0	8·0	220±5	1·5	118
	—	100	—	—	—	—	152	11·0	10·0	220±5	1·5	121
	—	100	—	—	—	—	152	11·0	12·0	220±5	1·5	129
	—	100	—	—	—	—	152	11·0	14·0	220±5	1·5	137
	—	100	—	—	—	—	152	11·0	16·0	220±5	1·5	144
	—	100	—	—	—	—	152	11·0	18·0	220±5	1·5	opaque product
	—	—	100	—	—	—	142	10·3	8·0	220±5	1·5	124
	—	—	100	—	—	—	142	10·3	10·0	220±5	1·5	132
	—	—	100	—	—	—	142	10·3	12·0	220±5	1·5	146
	—	—	100	—	—	—	142	10·3	14·0	220±5	1·5	150
	—	—	100	—	—	—	142	10·3	16·0	220±5	1·5	150
Zn $(CO_3)_2$	100	—	—	—	—	—	155	17·3	12·0	260±5	2·0	122
	100	—	—	—	—	—	155	17·3	12·5	260±5	2·0	Blocked
	—	100	—	—	—	—	152	17·0	17·0	260±5	2·0	131
Zn $(OH)_2$	100	—	—	—	—	—	155	13·7	13·7	220±5	2·0	119
	—	100	—	—	—	—	152	13·4	13·4	220±5	2·0	118
	—	—	100	—	—	—	142	12·6	12·6	220±5	2·0	116

rosinates in mineral spirit at a concentration of 20% solid showed no sign of precipitation or sludge formation at the end of this period. The stability was further tested by exposing powdered rosinates to oxygen atmosphere. Fused and precipitated zinc rosinates prepared from sulphur-modified rosins showed no increase in weight while precipitated product prepared from unmodified rosin gained 2.1% in weight after 20 days.

Conclusions

Fusion of sulphur-modified rosins with different zinc compounds provides a simple method for the preparation of clear homogeneous fused zinc rosinates. The blocking difficulties are eliminated and higher proportions of zinc compounds can be incorporated up to a maximum of double the stoichiometric amount. Precipitated and fused zinc rosinates prepared from sulphur modified rosins are resistant to oxidation and show good solubility and solution stability in common paint and varnish solvents.

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