PREPARATION OF STABLE METALLIC SOAPS OF ROSIN ACIDS AND THEIR DERIVATIVES

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This paper deals with the preparation and properties of stable rosinates of aluminium, cadmium, cobalt, copper, lead and zinc by (i) double decomposition using abietic acid, Rosin WW, Rosin FF, oxidised rosin and abietic acids, and (ii) fusion method using rosin oil having different acid values. It has been found possible to prepare satisfactorily stable unmodified rosinates if the acid is not allowed to get oxidised prior to use and is taken up in the solvent as soon as precipitated in a hydrated form. The stability also depends on the nature of the metal and the order of metals for stability is manganese, cobalt, aluminium, cadmium and copper. Most stable and concentrated solutions however are obtained by fusion method using metallic acetates and rosin oil having acid value from 0 to 80. Rosin oil of higher acid values does not give satisfactory results and in case of aluminium, cobalt and zinc shows blocking tendencies.

Introduction

The cation in metallic soaps, which are compounds of metals and fatty acids, plays an important role in such uses as paint driers, mildew proofing, ceramic glazes, whereas the anion part determines the physical properties like melting point, particle size, solubility characteristics etc. Most of the industrial uses of these soaps depend on (1) the physical characteristics of the soap, (2) its ability to influence the characteristics of liquids in which it is dispersed, and (3) its ability to dissolve in certain organic solvents and to supply metal cation. Probably the largest quantities of soaps are used for purposes which depend on the available metal present. The usefulness of the metals depends upon their solubilities in oils and thinners and on the stability of the solutions on storage, which property depends markedly on the nature of the fatty acid used. The soaps of saturated acids like napthenic acid have excellent solubility and durability, whereas those of unsaturated acids like linoleates and rosin acids oxidise whether they are stored as such or as solutions in solvents and oils. The oxidation of the soaps causes them to become less soluble, so that when these soaps age they are no longer soluble in solvents or, if they are already in solutions, they precipitate.

Considerable work has been done by various authors on improving the stability of metallic rosinates: Lithman used catalysts like nickel, copper, platinum, palladium, for treating rosins and partially hydrogenated rosins to decrease their unsaturated character and prepared rosinates from the resulting products.[1] Polymerised rosin is used for preparing metallic soaps having better solubility and a metal content greater than its equivalent combining proportion. In this way the maximum percentage of lead is increased from 23.0 to 31.0%,[2] and of cobalt from 7.5 to 19.0%.[3] The heat treatment of rosin is carried out in the temperature range of 250 - 350°C. till its optical rotation in the solid state reaches the range of 30° - 50°.[4] Cobalt rosinate made from this modified product has a metal content of 19%. Condensation products of rosin with maleic anhydride[5] or with formaldehyde [6] also give metallic soaps with high metal contents and good solubility in solvents.

Since the various processes for modification of rosin to prepare stable rosinates require the use of imported chemicals, it was considered worthwhile to study conditions under which unmodified and stable rosinates could be prepared. Another possibility is to use derivatives which could be easily produced from rosin. The present paper is limited to a report on the successful preparations and properties of aluminium, calcium, cadmium, cobalt, copper, lead and zinc soaps by (1) double decomposition using abietic acid, Rosin WW, Rosin FF, oxidised rosin and abietic acids, and (II) fusion method using rosin oil having different acid values.

Materials

Abietic acid required for the work was prepared by a simple method already evolved by S. Siddiqui et al.[7] based on the addition of alcoholic hydrochloric acid to alcoholic solution of rosin at room temperature. This method gives a yield of about 70% of abietic acid of melting point 150-152°C. and on recrystallisation from alcohol a melting point 156 - 58°C. The source of rosin acids used for this investigation was rosin grade WW and rosin grade FF manufactured by Jallo Rosin and Turpentine Factory, Lahore. For oxidised acids, abietic acid powder or powdered Rosin WW was exposed to atmosphere for one month before use. Rosin oils of different grades varying in acid values from 10 to 120 were prepared in the laboratory by destructive distillation of Rosin WW at atmospheric pressure.

Precipitated Rosinates

The precipitated rosinates have been prepared by a double decomposition reaction between aqueous solutions of sodium rosinate and a water-soluble salt of the metal. The following procedure has been found to give satisfactory results:—

Warm solution of sodium rosinate (10%) and a warm metal salt solution (10%) are added at a constant rate to a bath of clear warm water which is being agitated. The flows are adjusted in such a way that there is always a slight excess of free acid during precipitation. The precipitated metallic soap is treated in one of three different ways.

(I) The metallic soap is not filtered but the slurry is shaken with mineral turpentine. The soap dissolves in the solvent which is separated from the aqueous layer by means of a separating funnel.

(II) The metallic soap is filtered, washed, dried in vacuum at 60°C. and dissolved in mineral turpentine at room temperature.

(III) The metallic soap is filtered, washed, dried at 100°C. and dissolved in boiling mineral turpentine, since these did not dissolve at room temperture.

The values for the metal contents of the abietates and rosinates of different metals are reported in Table 1.

TABLE 1.—METAL CONTENT OF ABIETATES AND ROSINATES.

Metal	%metal in abietate	%metal in rosinate
Cadmium	14.95	13.8
Cobalt	8.25	7.85
Copper	8.85	8.00
Lead	24.10	23.20
Manganese	7.75	6.95
Zinc	8.95	8.20

The solubilities of the soaps in mineral turpentine and the storage characteristics of the solutions are reported in Table 2. The percentage of insoluble matter in mineral turpentine refers to the amount of soap which does not dissolve at room temperature. The matter goes into solution on warming, but reseparates slowly on cooling in about 48 hours. From the results reported in this table it is clear that the stability of the solutions depends on (1) the nature of the acid, (2) the method used for preparation of the solution and (3) the nature of the metal. The best results are obtained when freshly precipitated abietic acid is used and the metallic rosinate which is precipitated in hydrated form is immediately taken up with the solvent. Of all the metals, manganese gives the most stable solution. The solution of cobalt soap remains clear but changes from a violet to brownish tinge. Next in order of stability are aluminium, cadmium, and copper soaps solutions. Lead and zinc soaps are insoluble in solvents and are therefore not listed in the table.

Fused Rosinates

The following procedure for the preparation of fused metal rosinates has been found to be satisfactory in most cases.

"Rosin oil is heated to 240 - 50°C., the metal compound is added slowly with sufficient time allowed for the added metal compound to react before another portion is added. When the full quantity of the metal compound has been added, the mass is cooled to 200°C. and diluted with mineral turpentine to adjust the solution to contain 50% solids."

All the metal rosinates showed good solubility in linseed oil and organic solvents and, with the exception of aluminium rosinate, all of them were soluble in mineral spirits in concentration up to 40 - 60% solids. The maximum metal content of fused rosinates using a metal oxide was found to be approximately the amount of metal that would react with the free COOH group available to form the metal rosinate. When a metal acetate is used, the maximum metal content is usually about equal to that required to form a mixed acetate-abietate. The solutions of fused rosinates prepared from rosin oil having acid values from 0 to 80 were completely stable on storage. The characteristics of the fused rosinates made from rosin oils having acid values from 0 to 80 are reported in Table 3.

The stability of these rosinates decreased as the acid value of rosin oil used increased from 80

TABLE 2.—CHARACTERISTICS OF METALLIC SOAPS OF ROSIN ACIDS.

Acid	Method of preparation	Solubility in mineral turpentine g./100 ml.	%Insoluble in mineral turpentine (room temp.)	Stability of solutions after 1	4	8 Weeks	16	32	52
Cadmium									
Abietic acid fresh	I	6–8	nil	clear	clear	clear	clear	clear	S1
	II	5–7	nil	clear	clear	S1	S2	S2	S3
	III	8–10 (hot)	94–95	S1	S2	S3			
Rosin W W	I	6–8	nil	clear	clear	clear	clear	S1	S1
	II	5–7	nil	clear	S1	S1	S2	S3	S3
	III	8–10 (hot)	96–98	S1	S2	S3			
Rosin F F and oxidised acids	I	4–5	2–4	S1	S2	S3			
	II	4–6	25–30	S1	S3				
	III	6–8 (hot)	99-100	S2	S3				
Cobalt									
Abietic acid fresh	I	18–20	nil	clear	clear	clear	clear	clear	clear
	II	14–16	4–6 ..	clear	clear	clear	S1	S1	S2
	III	20–22 (hot)	96–98	S1	S3	—	—	—	—
Rosin W W	I	18–20	nil	clear	clear	clear	clear	clear	S1
	II	10–12	8–10	clear	clear	S1	S2	S3	—
	III	18—20 (hot)	98–100	S2	S3	—	—	—	—
Rosin F F and oxidised acids	I	12–14	8–10	S1	S3	—	—	—	—
	II	8–10	20–25	S2	S3	—	—	—	—
	III	16–18 (hot)	99–100	S2	S3	—	—	—	—
Copper									
Abietic acid fresh	I	8–10	5–6	clear	clear	clear	clear	clear	S1
	II	6–8	12–14	clear	clear	clear	clear	S1	S1
	III	10–12 (hot)	98–99	S1	S3	—	—	—	—
Rosin W W	I	8–10	10–12	clear	clear	clear	clear	clear	S1
	II	6–8	16–18	clear	clear	clear	clear	S1	S2
	III	10–12 (hot)	98–99	S1	S3	—	—	—	—
Rosin F F and oxidised acids	I	4–6	12–14	S1	S2	S3	—	—	—
	II	4–6	25–30	S1	S3	—	—	—	—
	III	6–8 (hot)	99–100	S2	S3	—	—	—	—

TABLE 2.—CHARACTERISTICS OF METALLIC SOAPS OF ROSIN ACIDS—*contd.*

Acid	Method of preparation	Solubility in mineral turpentine g./100 ml.	% Insoluble in mineral turpentine (room temp.)	Stability of solutions after 1 (Weeks)	4	8	16	32	52
Manganese									
Abietic acid fresh	I	5–6	4–5	clear	clear	clear	clear	clear	clear
	II	5–6	12–14	clear	clear	clear	clear	clear	S_1
	III	9–10 (hot)	98–99	clear	S_1	S_2	S_2	S_3	
Rosin W W ..	I	5–6	5–6	clear	clear	clear	clear	clear	clear
	II	5—6	12–14	clear	clear	clear	clear	S_1	S_1
	III	8–10 (hot)	98–99	S_1	S_2	S_2	S_3	—	—
Rosin F F and oxidised acids	I	4–5	10–12	clear	clear	S_1	S_1	S_2	S_2
	II	4–5	18–20	clear	S_1	S_2	S_2	S_3	—
	III	7–8 (hot)	98–99	S_2	S_3	—	—	—	—

S_1, S_2 and S_3 signify separation of 5–15%, 20–30%, 50% of the total soluble solids, respectively.

TABLE 3.—CHARACTERISTICS OF FUSED ROSINATES.

Acid value of rosin oil	Metal compound	Per 100 parts rosin oil: Metal compound parts by	Stoichometric amount metal compound	% metal in finished product
12	$Al(OH)(C_2H_3O_2)_2$	9.0	1.27	1.50
50	,,	14.0	5.30	2.33
75	,,	25.0	8.00	4.15
12	$Cd(C_2H_3O_2)_2 \cdot 2H_2O$	7.0	2.97	2.95
50	,,	25.0	12.40	10.50
75	,,	50.0	18.68	21.00
12	$Ca(C_2H_3O_2)_2 \cdot 2H_2O$	9.0	1.94	2.04
50	,,	17.0	8.10	3.86
75	,,	25.0	12.15	5.67
50	$Ca(OH)_2$	2.90	3.33	1.60
75	,,	3.60	4.50	1.96
12	$Co(C_2H_3O_2)_2 \cdot 4H_2O$	8.0	2.69	1.87
50	,,	19.0	11.32	4.55
75	,,	24.0	16.90	5.94
12	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	8.0	3.29	4.37
50	,,	20.0	13.80	10.92
80	,,	40.0	22.00	21.98
50	PbO	7.80	7.92	7.24
75	,,	11.55	11.88	10.70
12	$Zn(C_2H_3O_2)_2 \cdot 2H_2O$	14.0	2.32	4.15
50	,,	23.5	10.90	7.00
75	,,	35.0	14.55	10.6

upwards. Aluminium, cobalt and zinc acetates showed blocking tendencies in the course of the reaction: after certain amount of these salts had been added, there was a sudden formation of a heavy precipitate, which is insoluble in mineral spirits. These results for aluminium, cobalt and zinc are reported in Table 4.

TABLE 4.—BLOCKING PROPERTIES OF FUSED ROSINATES.

Acid value of rosin oil	Metal compound	Metal compound per 100 parts rosin oil	Remarks
120	$Co(C_2H_3O_2)_2 \cdot 4H_2O$	16.5	Blocked; heavy precipitate
120	$Al(OH)(C_2H_3O_2)_2$	15.2	Blocks; gels and precipitates
120	$Zn(C_2H_3O_2)_2 \cdot 2H_2O$	28.5	Blocks; heavy precipitate

Conclusions

The above experiments show that it is possible to prepare satisfactorily stable unmodified rosinates with metal content corresponding to the amount that would react with the free COOH group if the acid is not allowed to get oxidised prior to use and is taken up in the solvent as soon as precipitated in a hydrated form. Of course, the stability also depends on the nature of the metal, and the order of metals for stability is manganese, cobalt aluminium, cadmium and copper. Most stable and concentrated solutions however are obtained by fusion method using metallic acetates and rosin oil having acid value from 0 to 80.

These results also indicate that when completely unoxidised material is taken up in organic solvents, the solutions have a very high stability and oxidation is almost completely arrested. On the other hand if any considerable degree of preliminary oxidation has taken place before the rosinate is dissolved, the formation of solution does not prevent or noticeably slow down further oxidation. This second observation marks an extension of the previous theoretical discussions on instability and merits further quantitative work which may lend to elucidation of the precise mechanism of the instability of metallic rosinates.

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