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SULPHUR MODIFIED ROSIN-MALEIC ADDUCTS

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The preparation and properties of sulphur-treated rosin - maleic adducts and their esters have been studied. It has been found that oxidation characteristics of sulphur - treated rosins are markedly imparted to such products. Comparison of the properties of these resins with corresponding resins based on unmodified rosin is presented in this paper.

Key words: Sulphur modified rosin, Maleic adducts, Oxidation resistance; Blocking

INTRODUCTION

Sulphur modified rosin - maleic adducts. In a previous communication [1], we have described that the treatment of rosin with sulphur under appropriate condition reduces the oxidation properties to negligible proportions. The advantages achieved in sulphur modified rosin were also shown to be carried through when used in the preparation of metal rosinates [2-4] with the elimination of blocking tendencies generally encountered in fusion process. Esters of maleic treated rosin usually called 'maleics' are prepared from a combination of rosin with maleic anhydride and then esterifying the Diels-Alder adduct with a polyvalent alcohol. Maleics are commercial products widely used in coating and printing ink formulations with reduced unsaturation and improved oxidation properties. Present studies have been undertaken for further improvement in maleic adducts and their esters through sulphur treated rosin.

EXPERIMENTAL

A detailed description for preparing modified rosins using varying amounts of sulphur has already been reported [1]. The characteristics of these resins used in present studies are given in Table 1.

Preparation of maleic adduct. Sulphur-treated rosin was charged in batches of 500 g in a 1-litre four-necked round bottomed flask provided with a stirrer, thermometer, nitrogen inlet and a distillation connection. It was heated to 160° in an inert atmosphere before the addition of maleic anhydride.

Maleic anhydride was added as rapidly as possible. When the desired amount had been added, the temperature rose to 200° without the addition of external heat. This temperature was taken as the starting point of the reaction and was maintained till a product of constant softening point was obtained. Samples were removed at regular intervals and used for the determination of progress of reaction, softening points, acid and saponification values and oxygen absorption. The quantity of maleic anhydride more than 10 phr was avoided as the resulting products tended to be darker in colour. To determine if characteristics are further imparted to its derivatives, glycerol and pentaerythritol esters were prepared at 270-80°. Comparative runs were also made using untreated rosin. Table 2 presents data on reaction conditions and properties of various combinations carried out during studies.

Unreacted maleic anhydride was determined by dissolving samples in benzene followed by extraction with water and titrating aqueous solution with standard alkali. Oxygen absorption was assessed by exposing 2 g. samples of powdered material (passing 120 mesh) to oxygen atmosphere for a total period of one year and the increase in weight recorded with lapse of time. Control tests were also performed upon corresponding products of rosin.

RESULT

Table 3 shows the percent increase in weight with lapse of time for maleic addition products and their esters

Table 1. Characteristics of sulphur - treated rosins.

Parts of sulphur/100 parts of rosin	Acid value	Saponification value	Iodine value (Hanus)	Softening point (ring and ball) °C
2.5	154	160	159	74
5.0	152	157	120	72
7.5	142	150	84	69
–	*165	*172	*250	*75

*Untreated rosins.

Table 2. Preparation and properties of unesterified and esterified maleic adducts of sulphur – treated rosins.

Adduct No.	Gum rosin (g)	Sulphur-treated rosin (g)			% by weight of sulphur-treated rosin			Acid value	Saponification value	Softening point (ring and ball) °C
		2.5% S	5.0% S	7.5% S	Maleic anhydride	Glycerol	Pentaerythritol			
1		500			5			173	195	92
2		500			7.5			212	–	96
*3		500			10.5			193	240	99
4		500			5	10		15.7	–	112
5		500			5	–	11	43.4	–	122
6			500		5			173	197	90
*7			500		10	–	–	203	237	100
8			500		5	10	–	11.0	–	111
9			500		5		11	35.4	–	120
10				500	5	10	–	10.2	–	117
11				500	5	–	11	38.0	–	119
12	500				5	–	–	183	208	94
13	500				10	–	–	206	251	102
14	500				5	10.5	–	24.4	–	114
15	500				5	–	12	44.9	–	125

Rosin/treated rosin - maleic reaction temperature, 200°
Total reaction period, 4 hr.
Subsequent esterification temperature, 270 -80°: reaction period 3 hr.
* Acid value of aqueous extract : resin No. 3, 1.8, No. 7, 2.0

using rosins of varying sulphur proportions. The period of observation extended to one year. The oxidation resisting character of sulphur-treated rosin is markedly imparted in maleic adducts and derivatives. Adduct No. 6 prepared from 5% sulphur-treated rosin did not show increase in weight after one month against an increase of 3.12% in the corresponding product based on untreated rosin. The striking improvement was observed in products based on 7.5% sulphur which remained practically unaffected to oxidation after a period of four months. In general such products exhibit a high level of resistance to oxidation to an extent ranging between 0.5 to 0.9% increase in weight after one year against a figure of about 5% for corresponding product based on untreated rosin at the end of this period.

Under the conditions brought about, maleic anhydride reacted with sulphur-treated rosins in less than one hour without significant amount of free anhydride in water extracts. Acid value as low as 2, of aqueous extract corresponds to 0.17% of free anhydride against incorporation of 10 g per 100 parts resin. The softening points rose as maleic anhydride was increased from 5 to 10 phr. However, quantities above 10 phr were avoided as softening points showed a decreasing tendency.

Table 3. Comparative oxygen absorption of esterified/ unesterified adducts of sulphur – treated rosins and corresponding rosin products

Adduct No.	% total increase in weight of sample after, months					
	1	2	3	4	8	12
1	0.09	0.14	0.17	0.24	0.55	0.90
4	0.08	0.11	0.15	0.23	0.57	0.92
5	0.02	0.07	0.11	0.17	0.51	0.81
6	Nil	0.020	0.041	0.100	0.392	0.76
8	Nil	0.025	0.046	0.101	0.410	0.77
9	Nil	0.008	0.008	0.095	0.380	0.62
10	Nil	Nil	Nil	0.046	0.26	0.59
11	Nil	Nil	Nil	Nil	0.26	0.56
12	3.12	3.18	3.2	3.3	4.50	4.83
14	3.00	3.12	3.3	3.3	4.86	5.01
15	2.83	2.93	3.1	3.5	4.41	4.82

The sulphur-treated rosins show a measurable reduction in acid value compared to rosin (Table 1). By virtue of

lower initial acid values, the esterified maleic adducts so prepared achieve a low level of acid value with the use of lesser quantities of polyhydric alcohols than required for corresponding rosin products. It was also found that softening points of these products were lowered by 2-4° probably due to lower initial values observed in sulphur treated rosins. The adducts were soluble in aromatic solvents, fully compatible with mineral oil, and easily dispersable in drying oil when heated above 200°.

CONCLUSION

Addition products prepared by reacting maleic anhydride with sulphur-treated rosins and subsequent esterification with glycerol or pentaerythritol yield improved products with respect to oxidation resistance compared to corresponding rosin products. It is concluded that use of these resins in coating and printing ink as a vehicle will result in the formulation of improved performance.

REFERENCES

1. A.M. Ahsan, M. Aslam and Salim Akhtar, Pakistan J. Sci. Ind. Res., 7, 9 (1964).
2. Salim Akhtar, S.A. Mehdi and M.A. Hashem, Pakistan Pat. 122, 786 (1972).
3. Salim Akhtar and S.A. Mehdi, Pakistan J. Sci. Ind. Res., **15**, 335 (1972).
4. Salim Akhtar and S.A. Mehdi, *Ibid,* **17**, 239 (1974).