impurities to be removed. The only by-product is water. The process is direct, does not require large volumes of materials which must later be discarded, and employs the metal itself, usually an economical raw material. The only disadvantage is that it is not as rapid as the fusion process. Cobalt and iron tallate driers are manufactured by the direct metal reaction process.

Application

In general, tallate and naphthenate driers at the same metal content dry paint with equal efficiency. Slight advantages may be found for each drier line in specific paints, but these differences seldom vary by more than 10% of the total drying time.

Other variables affecting the drying time of a paint or enamel, such as temp, humidity, air circulation and others, may cause a 50% deviation in drying time. A temp variation of 20 degrees (68–88F) has been known to cause wide differences in the drying time of an enamel.

Technical journals are replete with data concerning physical properties of driers and methods of manufacture, but very little has been published in the past ten years comparing the relative efficiency of driers made from different anions.

Available data comparing tallate and naphthenate driers indicate no special problem in converting from one drier system to another. Minor differences in color, viscosity and non-volatile content of the driers become insignificant when reviewed from the aspect of total effect on finished paint properties. For example the degree of variation of viscosity of one batch of paint to the next is often significantly larger than any variation produced by the change in drier.

Table II shows that tallate driers may be used in a multitude of paint systems ranging from linseed oil house paints to the more modern finishes, such as one-package urethanes. While drying times vary considerably among the coatings tested, very little difference in drying time is noted between paints containing naphthenate and tallate driers.

Comparison of the efficiency of the three major types of driers are shown in Table III. The figures shown represent the average of three determinations run on three separate days. It is evident that the tallate driers are equivalent in drying efficiency to naphthenate and octoate (2-ethylhexoate) driers. The comparisons made in Tables II and III show that the selection of the anion plays a minor role in the overall efficiency of metal driers in the coatings industry.

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The Relationship of the Dimer Content of Rosin Determined by Gas Chromatography to Crystallization Time

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Abstract

The resin acid dimer content of rosin influences the crystallization time, as determined with the Burrell-Castor Gelometer. A gas chromatographic packing prepared by treatment of Chromosorb W with dimethyldichlorosilane and trimethylchlorosilane resolved the methyl esters of rosin dimers into 15 components. A vacuum stripping method for assay of rosin dimer agrees with results obtained by quantitative gas chromatography.

Introduction

METHYL ESTERS of rosin can be analyzed for resin acid composition by gas chromatography upon polyester (1) or nitrile silicone gum rubber (2) packings. The methyl esters of fumaric and maleic adducts of resin acids can be chromatographed upon short columns packed with a 2% liquid phase of silicone gum rubber (3). The methyl esters of resin acid dimers have not been eluted from these columns.

Packings prepared by coating Chromosorb® support with siloxane permitted the elution of methyl esters of resin acids, resin acid adducts and resin acid dimers and consequently their determination. Both dimethyldichlorosilane and hexamethyldisilazane (4,5) have been extensively employed to reduce tailing of samples chromatographed on diatomaceous supports. The analytical results obtained by gas chromatography were confirmed by a vacuum stripping method.

One method of reducing or eliminating the tendency of tall oil rosin to crystallize is by increasing its dimer content. Crystallization tendency can be measured by oven, refrigeration and solution techniques. Each of the preceding methods is difficult to quantitate because of the human error in judgment involved in fixing the exact crystallization time. The acetone crystallinity method of Palkin and Smith (6) yields relative crystallization rates in a short time although subject to the judgment error. A method has been devised which uses the Burrell-Castor Gelometer. The Gelometer employs a thermostatted bath with a slowly rotating probe connected to a microswitch and timer. When the sample crystallizes, a sharp increase in viscosity of the mixture stops the probe at a preset torque value. No operator attention is required.

Experimental Procedures and Data

Chromatographic packing was prepared by adding 0.8 ml of dimethyldichlorosilane and 0.2 ml of trimethylchlorosilane to 2 g of 60–80 mesh Chromosorb W. This mixture was held in a closed vial for six weeks at room temp. After reaction, the polysiloxane-coated product was treated briefly with 25 ml of boiling methanol, drained and dried.

The chromatographic column was a 76 cm x 0.318 cm OD (0.05 cm wall) 304 stainless steel tube. This

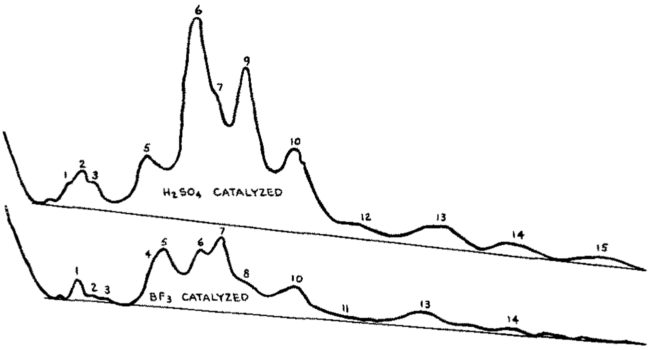

FIG. 1. Chromatograms of methyl esters of rosin dimer at 260C.

was packed by vibration with 60–80 mesh siloxaned packing. Columns were conditioned 1–3 hr at 340–350C at a nitrogen flow of 16 ml/min.

The injection tube and the flame ionization detector were mounted on a metal block capable of being heated to 360–370C. Metal cooling fins on the septum nut aided in the dissipation of heat, which, at ca. 350C, caused an increase in bleed from decomposition of the septum. A 50–100 μg sample of methyl esters, contained in 0.2–0.8 μl of benzene, was injected.

The vacuum stripping method was carried out by measuring the loss in wt of a 0.1-g sample. The sample in a combustion boat was placed in a 33 cm furnace set at 225C. The 2.2-cm diam furnace tube was connected to a vacuum system ballasted at 450 μ with ethylene glycol at 25C. The sample was held under these conditions for one hr and removed to an atmosphere of nitrogen for cooling.

Crystallization experiments with the Burrell-Castor Gelometer were made with the oil bath at 110C. The stirring probe was set and calibrated so that a thread wrapped around the 5-mm diam shaft would lift a 60-g wt but would shut off the timer and motor with a 70-g wt. The stirring probe measured 6 mm x 178 mm by 0.8 mm and rotated at 10 rpm. The sample tube was a 18 mm x 150 mm Gardner tube filled to a depth of 35 mm with molten rosin.

Standard samples of maleopimaric acid, fumaropimaric acid and other resin acids were furnished by the U.S. Department of Agriculture, Naval Stores Station, Olustee, Fla. Dimer acids were prepared by H_2SO_4 and BF_3 polymerization. The methyl esters of resin acids, adducts and dimers were made with diazomethane (7).

TABLE I

Relative Retention Times of Methyl Esters Rosin and Rosin Derivatives on TMS-DMS Column

Component	210C	260C
Dextropimarate	0.12	......
Levopimarate	0.15	......
Dehydroabietate	0.16	......
Abietate	0.18	......
Neoabietate	0.26	......
Fumaropimarate	1.0 [a]	1.0 [b]
Maleopimarate [c] (minor)	1.3	......
(main)	1.5	......
Resin acid dimer esters		
1	......	5.2
2	......	6.0
3	......	6.6
4	......	8.8
* 5	......	9.1
* 6	......	11
* 7	......	12
8	......	14
* 9	......	16
*10	......	19
11	......	20
12	......	22
13	......	24
14	......	26
15		31

* Major dimer components.
[a] = 15.2 min.
[b] = 1.5 min.
[c] = Proportions depend upon esterification time.

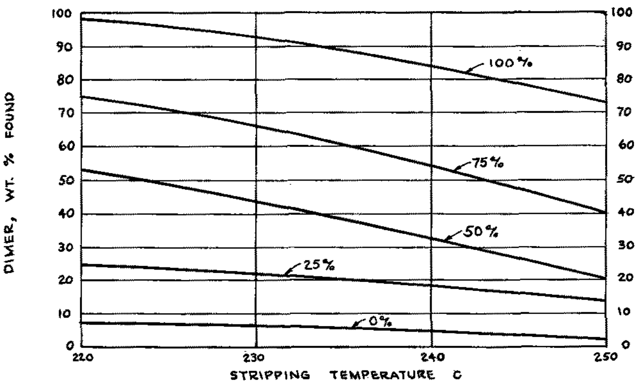

FIG. 2. Gravimetric Method for rosin dimer.

Results

Figure 1 shows chromatograms of BF_3 and H_2SO_4 dimerized rosins. These isothermal chromatograms show that although components of the two dimers exhibit the same retention times, the relative proportions are different. Resin acids are eluted with the solvent under these conditions. A total of 15 substances was found.

Relative retention times at 260C of these dimers with respect to fumaropimarate are shown in Table I. The relationship of resin acid methyl esters at 210C is included to show that resin acids and dimer acids can not be measured under a single set of isothermal conditions. It is necessary to temp program from 140–320C in order to determine the chromatogram area percentages of the resin acids and dimer acids. The fumaropimarate was taken as a reference (Table I) because the maleopimarate appeared as two peaks, the main peak comprising two-thirds of the material. The dimer samples prepared with BF_3 and H_2SO_4 show five major components and 10 minor ones.

A gravimetric assay procedure for dimer content was a vacuum stripping technique. Distilled tall oil rosin, a dimer standard obtained as a molecular distillation residue, and three blends of these were made for standardization purposes. Figure 2 shows the amt of residue in these five standards after being subjected to 450 μ for one hr at four different temp. From this information, 225C was selected as an optimum temp. At 225C, the results are slightly high for low dimer levels and slightly low for high dimer levels.

The relation of the chromatographic determination to the gravimetric determination is shown in Figure 3. The chromatogram areas were determined by weighing the paper. Much of the scatter in Figure 3 is attributed to the distillation analysis. The standard deviation of the chromatographic method is ±2 area percentage at the level of 40% dimer based on a quadruplicate determination and a duplicate determination. The distillation assay has a standard deviation of ±4 wt percentage at the 40% dimer level based on nine duplicate determinations.

The standard deviation of the crystallization time determined by the Burrell-Castor Gelometer is ±60 sec at the level of 500 sec based upon two triplicate determinations. It was not necessary to seed the sample to obtain reproducible results. Figure 4 depicts the crystallization time for various standard dimer

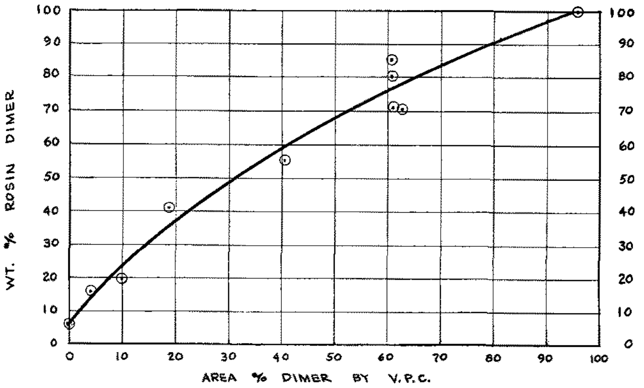

FIG. 3. Wt percentage rosin dimer vs. area percentage dimer.

mixtures. However, the method can not be used above 20% dimer content because of the high viscosity ranges that are encountered.

Figure 4 also shows the crystallization times of two samples analyzed for dimer. Tall oil rosin crystallizes in five min. Addition of 10% dimer lengthens the time to five hr and 20% dimer to ca. 10 hr. Wood rosin crystallizes in 30 min and American gum rosin requires more than 20 hr.

Discussion

Although the dimer content plays a role in the crystallization of tall oil rosin, factors other than dimer content control the crystallization rate of wood rosin and gum rosin.

Analysis of rosin adducts and dimers was done by gas chromatography using a polysiloxane coated column packing instead of the reported silicones (3). The support was prepared by bonding to the inorganic silicate short poly (dimethylsiloxy) chains which were terminated by trimethylsiloxy groups. The bound moisture, the bound metal, and hydroxyl content of the diatomaceous earth supplied both the necessary sites for anchoring chains and for the hydrolytic polymerization of the silyl chlorides. Methanol washing converted unreacted chloro groups to methoxyls but served primarily to remove unbound silane derivatives. The behavior of the column was essentially that of a very low level silicone gum column. Materials with mol wt up to 600 have been chromatographed on this packing.

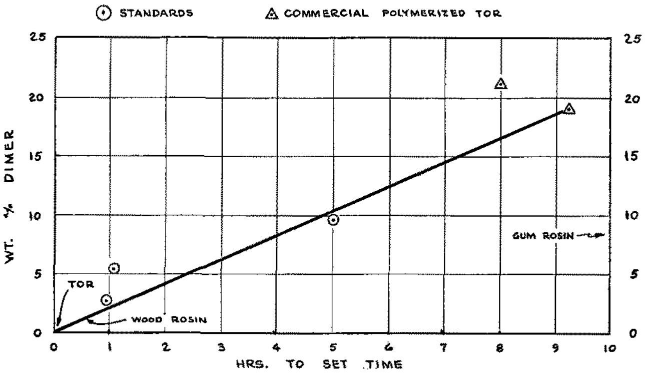

FIG. 4. Wt percentage dimer vs. set time.

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