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PAUL R. WATSON  
ALLENE JEANES  
CARL E. RIST

Northern Regional Research Laboratory  
Agricultural Research Service  
U. S. Department of Agriculture  
Peoria, Illinois

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### Graphical Presentation of Copolymer Composition

The relationship between copolymer composition and monomer composition is often shown in graphic form by a plot of  $F_1$  versus  $f_1$ , where  $F_1$  is the mole fraction of monomer 1 in the copolymer being formed at the instant when  $f_1$  is the mole fraction of monomer 1 in the unconverted monomer. In terms of relative reactivities,

$$\frac{F_1}{F_2} = \left(1 + \frac{r_1 f_1}{f_2}\right) / \left(1 + \frac{r_2 f_2}{f_1}\right) \quad \text{or} \quad Y = r_1 X \frac{(1 + r_1 X)}{(r_1 r_2 + r_1 X)}$$

where  $Y = F_1/(1 - F_1)$ ,  $X = f_1/(1 - f_1)$ , and  $r_1$  and  $r_2$  = relative reactivities.<sup>1</sup>

Usually the compositions are plotted as  $F_1$  against  $f_1$  on arithmetic coordinates similar to  $x, y$  diagrams for vapor-liquid equilibria. However, a diagram of  $\log Y$  versus  $\log X$

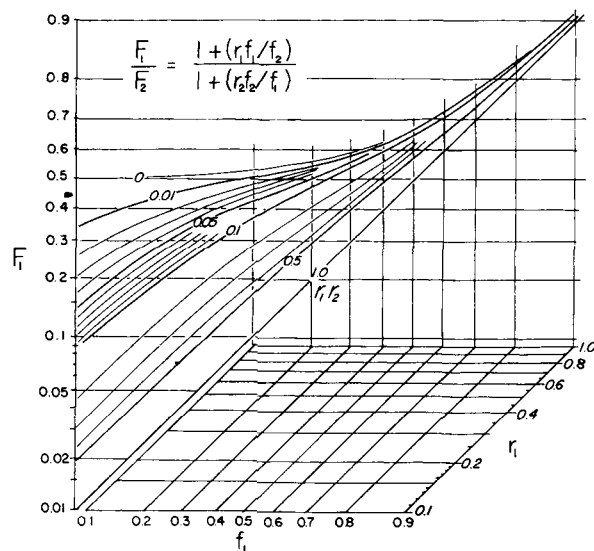


Figure 1

has several advantages. In the first place, "ideal" systems ( $r_1 r_2 = 1$ ) plot as straight lines with a slope of 1. Even systems with  $r_1 r_2 \neq 1$  show much less curvature and therefore require fewer calculated points to estimate completely. Moreover, since  $r_1$  and  $X$  appear together, a plot of  $\log Y$

versus  $\log X$  (when  $r_1 = 1$ ) is changed (from that when  $r_1 \neq 1$ ) merely by adding  $\log r_1$  to the abscissa.

In the second place, the  $\log X$ ,  $\log Y$  diagram can be used as a graphic solution for  $F_1$  as a function of  $f_1$ ,  $r_1$ , and  $r_2$ . In Figure 1, the abscissa and ordinate are labeled  $f_1$  and  $F_1$  although  $\log X$  and  $\log Y$  are actually plotted. The shifting of the  $f_1$  axis is done graphically by a logarithmic scale of  $r_1$ . Example: Copolymer composition ( $F_1$ ) desired when  $f_1 = 0.4$  for vinyl acetate (monomer 1) and vinyl chloride (monomer 2);  $r_1 = 0.23$ ,  $r_1 r_2 = 0.39$ . (a) Follow  $f_1$  (at bottom of figure) to intersection with  $r_1 = 0.23$ . (b) Move vertically to line for  $r_1 r_2 = 0.39$ , read  $F_1 = 0.24$ .

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F. RODRIGUEZ

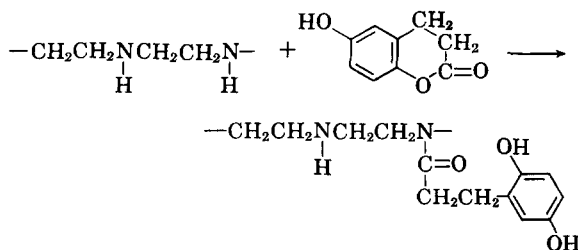
Geer Rubber and Plastics Laboratory  
Cornell University  
Ithaca, New York

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### A Convenient Preparation of a Hydroquinone Redox Polymer

Many types of polymers have been described in the literature known as either redox polymers, electron-exchange polymers, or nondiffusible reducing agents. Examples of these are polyvinyl hydroquinone,<sup>1,2</sup> copolymers of vinyl hydroquinone,<sup>3</sup> polyvinyl gentisal,<sup>3</sup> polyacrylylascorbic acid,<sup>3</sup> and poly-3-(2,5-dihydroxyphenyl)propylene oxide.<sup>4</sup>

Recently we have had occasion to prepare polymers containing the monosubstituted hydroquinone structure, linked by a chemical bond stable to concentrated alkali. Most of the polymers listed above are tedious to prepare, and we now wish to report a convenient synthesis of polymeric hydroquinones. The method involves the reaction of a polymeric primary or secondary amine with 2,5-dihydroxyhydrocinnamic acid lactone. An optimum polyamine is polyethyleneimine because the amine equivalent weight is low, resulting in a high hydroquinone content on a weight basis, and also because the resulting tertiary amide structure is quite stable to alkali.



### Experimental

The 2,5-dihydroxyhydrocinnamic acid lactone was prepared by conventional methods from 2,5-dimethoxybenzaldehyde and malonic acid followed by reduction and simul-

taneous demethylation and lactonization with hydrobromic acid, m.p. 159–160°C.<sup>4</sup>

In a typical preparation 14 g. of a 50% aqueous solution of polyethyleneimine (50,000 molecular weight) was allowed to react with 25 g. of 2,5-dihydroxyhydrocinnamic acid lactone in 200 cc. of a 50% methanol-water solution. The mixture was refluxed under nitrogen for 24 hr. and the product precipitated into acetone. After a second reprecipitation 8 g. of polymer was obtained.

The polymer was substituted to about 60% of the theoretical on the basis of carbon and nitrogen analyses. It was soluble in alkali and when exposed to air underwent many color changes associated with various oxidation states. The infrared spectrum showed no carbonyl absorption at 1730  $\text{cm}^{-1}$  associated with the lactone but a band at 1640  $\text{cm}^{-1}$  characteristic of an amide.

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LLOYD D. TAYLOR

Chemical Research Laboratories  
Polaroid Corporation  
Cambridge, Massachusetts

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### X-Ray Diffraction Studies of Indian Rubber Grade China Clays

Clays constitute an important class of compounding ingredients for rubber, both as fillers and reinforcing agents. Naturally occurring clay deposits widely differ in their mineralogical status and thus differ considerably in their behavior in rubber. Clays having a very high concentration of well crystallized kaolinite are found to be quite reinforcing when mixed with rubber,<sup>1</sup> while a deposit rich in finely crystallized halloysite has been claimed to exhibit reinforcement as good as HMF carbon blacks.<sup>2</sup> X-ray diffraction methods are commonly used to determine the mineralogical status of clays. This treatment was for the first time applied to the Indian rubber-grade china clays as a part of the work on their evaluation in natural rubber.<sup>3</sup> The clays undertaken for study were obtained from different parts of the country: Kendposi and Bhonda (Bihar), Appenhalli, Nandihalli and Thirthahalli (Mysore), Palyangadi and Kannapuram (Kerala), and Rairangpur (Orissa).

The x-ray diffractometer tracings were taken on a G.E. XRD-3 diffractometer unit, Cu  $K_{\alpha}$  radiation ( $\lambda = 1.54050$  A.) and a rate of scanning of  $2^{\circ}/\text{min.}$  being used. The other experimental conditions included, x-ray beam slit =  $1^{\circ}$  and x-ray counter slit =  $0.1^{\circ}$ . The diffractometer tracings are presented in Figures 1 and 2. For identification of various lines the A.S.T.M. standard card index<sup>4</sup> was used.

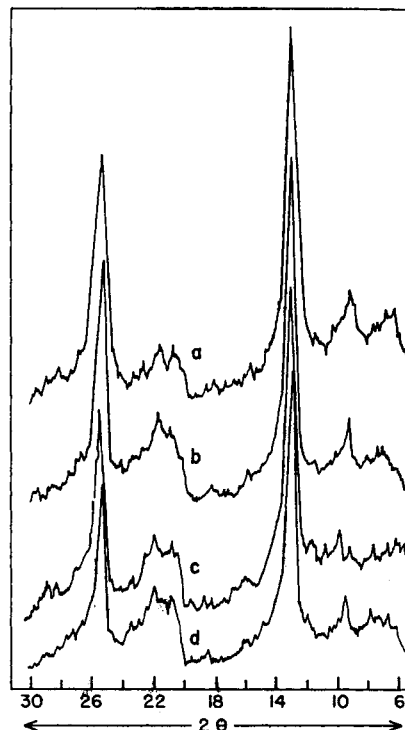


Fig. 1. X-ray diffractometer tracings of clays: (a) Nandihalli; (b) Kannapuram; (c) Thirthahalli; (d) Palyangadi.

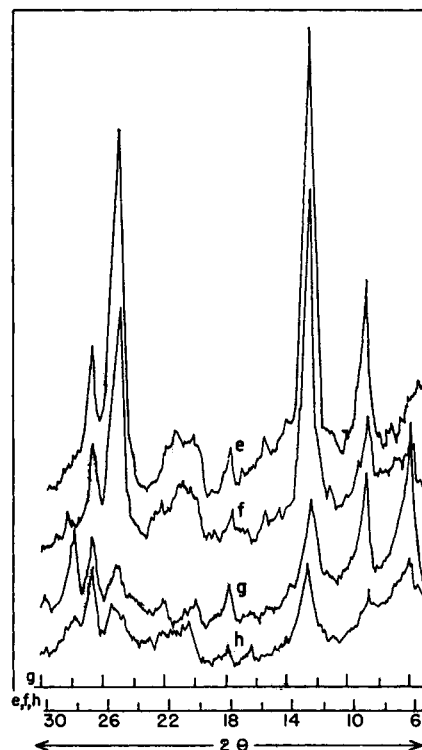


Fig. 2. X-ray diffractometer tracings of clays: (e) Appenhalli; (f) Rairangpur; (g) Kendposi; (h) Bhonda.