taneous demethylation and lactonization with hydrobromic acid, m.p. 159–160°C.[5]

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 cm.$^{-1}$ associated with the lactone but a band at 1640 cm.$^{-1}$ characteristic of an amide.

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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,[1] while a deposit rich in finely crystallized halloysite has been claimed to exhibit reinforcement as good as HMF carbon blacks.[2] 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.[3] 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_α radiation (λ = 1.54050 A.) and a rate of scanning of 2°/min. being used. The other experimental conditions included, x-ray beam slit = 1° and x-ray counter slit = 0.1°. The diffractometer tracings are presented in Figures 1 and 2. For identification of various lines the A.S.T.M. standard card index[4] was used.
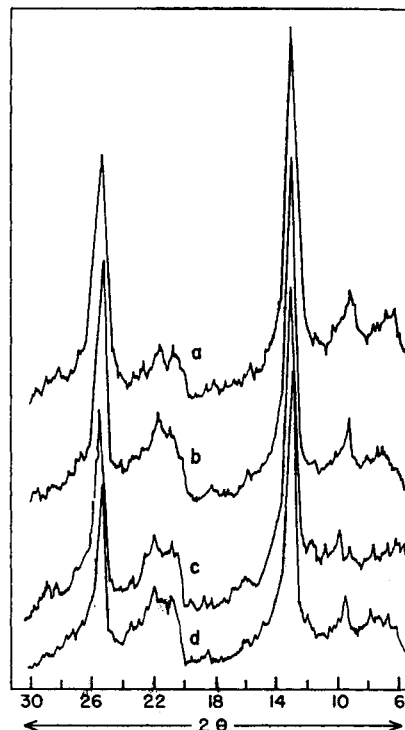

Fig. 1. X-ray diffractometer tracings of clays: (a) Nandihalli; (b) Kannapuram; (c) Thirthahalli; (d) Palyangadi.
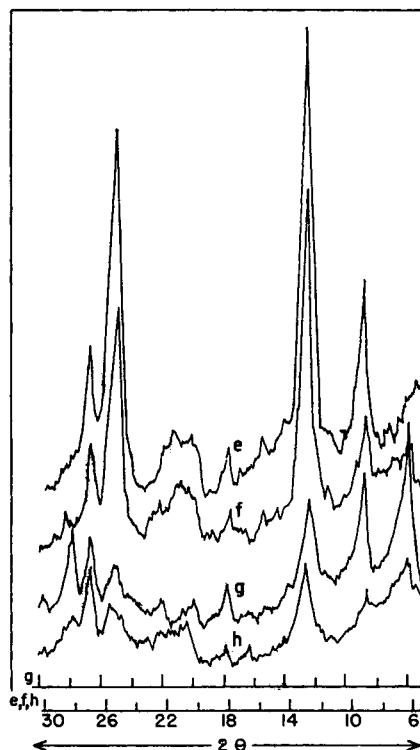

Fig. 2. X-ray diffractometer tracings of clays: (e) Appenhalli; (f) Rairangpur; (g) Kendposi; (h) Bhonda.

TABLE I
Clay Minerals Identified in Various Samples

Clay	Clay minerals
Kendposi and Bhonda	Mixtures of poorly crystallized kaolinite, montmorillonite, talc and muscovite
Appenhalli	Poorly crystallized kaolinite (about 70%), admixed with talc and illite
Nandihalli	Poorly crystallized kaolinite, traces of talc
Rairangpur	Dickite admixed with muscovite (about 15%) and traces of talc
Thirthahalli, Palyangadi, and Kannapuram	Well crystallized kaolinite

The clay minerals identified in these eight samples are given in Table I.

These clays were later compounded in natural rubber, and the properties of the rubber stocks were studied. The results indicate that Thirthahalli, Palyangadi, and Kannapuram clays exhibit superior compounding properties as compared to the rest, confirming the importance of the mineralogical status of rubber-grade china clays.

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Note on Colloidal Dispersions from Block Copolymers

Controlled addition of a selective nonsolvent to the solution of a block copolymer results in the "precipitation" of one of the components of the copolymer.[1] Aggregate formation is expected and has been reported in such instances. It seems reasonable to assume that clustering of like segments occurs, and that the resulting aggregate is maintained dispersed by the blocks still soluble in the solvent–nonsolvent mixture.

If the aggregate formed is constrained to contain primarily one kind of block, then the colloidal particle should possess a limiting size. Subsequent removal of solvent will cause collapse of the other block component to form a shell around the original aggregate core.

Addition of acetonitrile to benzene solutions of polystyrene–poly(methyl methacrylate) (PS–PMMA) block copolymers causes formation of such colloidal dispersions. When the copolymer composition is roughly 1:1, a highly turbid solution develops at a solvent composition corresponding to about 55% acetonitrile. The intrinsic viscosity exhibits a pronounced decrease at this solvent composition as is shown in Figure 1. The same level of acetonitrile when added to benzene solutions of PS homopolymer causes polymer precipitation. These experiments indicate that the addition of acetonitrile causes collapse of the PS chains which may be accompanied by micelle formation. Solubility of the PMMA chains in the solvent-nonsolvent mixture prevents phase separation.

Dilution of an (80:20) acetonitrile–benzene mixture at constant solvent composition followed by evaporation to produce specimens suitable for viewing by electron microscopy yields colloidal particles of spherical shape as demonstrated by Figure 2. The diameter of these particles varies with the molecular size of the copolymer (See Table I).

TABLE I
Particle Sizes of Some Colloidal Dispersions

Copolymer preparation	How dispersion formed	$\bar{M}_{total}$	$\bar{M}_{PS\ block}$	Chrome shadowed	Diameter, A.
1	Direct in CH₃CN	169,000	76,000	No	550
2	Direct in CH₃CN	(350,000)	(175,000)	Yes	1230
2a	Pption from C₆H₆ with CH₃CN	"	"	Yes	1050
2b	"	"	"	No	735

With PS–PMMA block copolymers, dispersions may also be produced by direct peptization of the dried polymer in acetonitrile, followed by dilution and evaporation as above. The particles thus formed were found to be similar in size to those formed by selective precipitation (see entries 2 and 2a in Table I); small differences are probably due to variations in the amount of chrome shadowing.

Since the acetonitrile is a nonsolvent for PS and a poor solvent for PMMA, it appears that dispersions formed either by precipitation, involving collapse of the PS component first, or by direct dispersion should produce a colloidal aggregate of many chains with the PMMA on the surface and the PS at the core.