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Plumbite-Treated Cotton in Formation of Glassy Materials

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Synopsis

Glass-like materials containing carbon were produced by heating plumbite-treated cotton fabrics in a limited oxygen atmosphere while in contact with a surface having a high silica content. Although the new materials were changed to a clear glassy state, they retained the design and shape of the fabric weave and were hard, brittle, acid resistant, and alkali resistant. Surface smoothness of the new materials and release from the high silicon-content materials on which they were made depended on lead content of the plumbite-treated cotton fabric. High lead contents produced smoother surfaces and better release. This information was applied in producing glass-like write-on labels for laboratory glassware or individual flakes of the new material. Direct heat from a Bunsen-type burner caused the new glass-like materials to become metallic gold in color without altering other properties. Indirect heat reversed the color to the original. ESCA and x-ray fluorescence examinations showed the atom ratio of lead to silicon to be 2.5:1 for materials made from low lead-content fabrics and 0.5:1 for those made from high lead-content fabric. Substantial carbon was present in all lead levels.

INTRODUCTION

This report concerns interesting glassy materials which were produced by heating sodium plumbite-treated cotton fabric in contact with a source of silicon. Analyses indicate that the new glassy materials may contain considerable amounts of carbon. They are resistant to strong acids and alkalis, are hard, withstand the heat of a Bunsen flame (~1200–1500°C), can be produced as write-on labels for Pyrex-type glassware, are temperature and chemical resistant, and can serve as adhesives between glasses, as decorations, or as gold-colored coating.

Since "glasses" are composed of many repeating units, in the broadest sense they may be called polymers, and many polymers are glass-like. Usually, glass is not made by using carbon, whereas polymers are made by using carbon compounds. The new materials described in this report seem to exhibit characteristics of both glasses and polymers.

Although glass appears solid, it is technically a supercooled liquid. Glasses contain silicon and oxygen and may contain other materials, particularly metal. Carbon has been used in trace amounts as a coloring agent or to produce black foamed glass. In neither instance was carbon necessary to the formation of a glass. Carbon contained in the cotton was required for formation of the new chemical structure and the fabric weave patterns and shapes

that were retained in the new products. Lead oxide has been widely used in pottery glazing and to make lead, flint-type glass. It has also been used in the manufacture of solder glasses used for joining glasses and/or metals. The solder glasses contain no carbon, have no visible structure, soften at low temperatures, and are not very resistant to chemical attack.

Carbon is, of course, a common structural element of polymers and may also be used as a filler or to add tensile strength. Silicone polymers are well known, but lead or other metals are not prominent in polymer technology.

EXPERIMENTAL

Treatment of Fabric. The procedure for treating the cotton fabric used in making the new glassy material has been described previously.[1] Briefly, it consisted of soaking the fabric in an aqueous solution of sodium plumbite prepared by the method of Griffin,[2] washing out the excess plumbite solution, and drying the fabric. The amount of lead added was readily varied from a few per cent to about 40 per cent (by weight) of the treated fabric by varying the time the fabric was exposed to the plumbite solution.

Basic Procedure. The basic process for production of the glassy material involved heating the plumbite-treated fabric to a temperature of 600°C while the fabric was in surface contact with a material having a high silicon content, such as a glass or porcelain. The temperature of 600°C was maintained for about 1 hr. The fabric had been placed in contact with the silicon material prior to commencement of heating, and the heating was carried out in a muffle furnace which supplied even heat and somewhat limited oxygen.

As heating commenced, the fabric sample became black and then yellow before changing into a glassy form. When either the silicon material or the oven was at reaction temperature upon introduction of the treated cotton, or when the oven door was kept open, the fabric burned, producing metallic lead rather than the glass-like material.

Formation of the new material involved several recognizable steps. The plumbite-treated fabric first turned black, indicating a carbon skeleton. Further heating turned the skeleton greenish yellow. In this state it often appeared as if some electric charge attracted it toward the glass on which it rested. Further elevation of temperature caused the fabric skeleton to adopt glass-like properties.

ANALYSES

Lead contents of the sodium plumbite-treated cotton fabrics were determined by x-ray fluorescence,[3] using disks of ground material. Composition of the surfaces of the new glassy materials was determined by electron emission spectroscopy (ESCA).[3] This procedure is effective to a depth of about 50 Å. ESCA not only provides a means for measuring the presence and quantity of an element, but permits differentiation of various oxidation or combining states of the elements.

Scanning electron micrographs were made using techniques reported in the literature.[3]

Thermogravimetric analysis was used to detect loss of weight as the fabric sample was heated to form the new glassy material and as the new glassy material was heated to 1200°C.[3] This technique was used to determine the temperature at which carbon from the fabric matrix was lost.

Flakes of the new glassy materials were immersed in strong acidic or basic solution to extract loosely held lead. Lead contents of the solutions were determined by atomic absorption.[3]

F-Centers as a source of color[4] were investigated by irradiating the glassy materials with high-energy sources. Samples were irradiated in the SRRC cobalt-60 radiation source to a dosage of 1 megarad, or they were irradiated with ultraviolet energy in a Rayonet RPR-100 photochemical chamber reactor at either 3500 Å using an intensity rated at 9200 microwatts/sq cm with 1.5×10^{16} photons/sec/cm^3, or 2537 Å using an intensity rated at 12,500 microwatts/cm^2 with 1.65×10^{16} photons/sec/cm^3. Length of exposure to ultraviolet energy varied from 10 min to 6 hr.

RESULTS AND DISCUSSION

Samples of 80 × 80 cotton printcloth were treated with aqueous sodium plumbite solution to obtain lead contents of 4%, 6%, 8%, 13%, 16%, 20%, 24%, and 37% by weight. These treated fabrics were placed on porcelain or Pyrex-type glasses and heated as described in the experimental section. All of the samples formed glassy materials. Those with lead contents of 4% through 16% adhered tenaciously to the surface on which they were produced and maintained the same shape and pattern as the treated fabric from which they were made.

For example, Figure 1F is typical of a label formed on a porcelain spatula. When the lead content of the cotton fabric was on the order of 20% or higher, the glassy product separated in flakes from the silicon glass on which it was made. Figure 1E illustrates the separation of the new glass from a porcelain substrate. The flakes were hard enough to scratch soft soda lime glass or stainless steel. They lost no detectable weight when soaked 24 hr in either concentrated HCl, HNO_3, H_2SO_4, aqua regia, or 50% NaOH. The solutions used for soaking were found by atomic absorption to contain up to about 20 ppm of lead, which is an extremely small amount. When flakes were subjected to the direct flame of a Bunsen burner (~1200–1500°C), they did not lose their shape or sharp edges.

The fabrics with 6% to 16% lead formed a translucent glassy material on the surface of any high silicon-content substrate, as illustrated in Figure 2. The translucent glassy products adhered firmly and had both the shape and weave of the fabric used. Such products serve as labels of any size, or they can be written on with an ordinary pencil and the writing erased with an ordinary rubber eraser.

In Figure 3 are scanning electron micrographs of the surfaces of the glassy label at low (A) and high magnifications (C). Similar micrographs of separated glassy flakes at low and high magnification are illustrated in B and D, respectively. The rough fibrous character of the label is evident in A, and the regularity of the fabric pattern shows in the high magnification of C. The flakes are of a relatively smooth surface, and therefore the fiber pattern

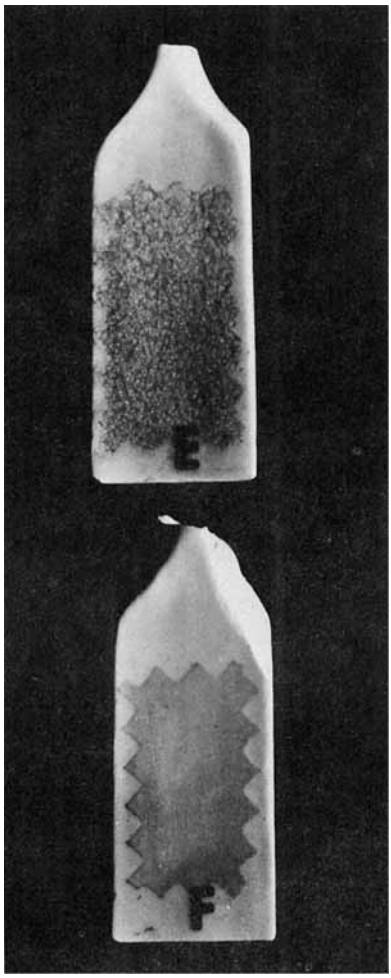

Fig. 1. Glassy materials from plumbite-treated cotton print cloth on porcelain: (E) from cotton having 37% lead; (F) from cotton having 8% lead.

is difficult to ascertain (B). High magnification (D) reveals two holes and many small black specks. There are also some fracture lines due to the stresses induced during cooling of the glassy material and its original glass substrate.

Since low lead-content plumbite-treated cellulose adhered firmly to different glasses, it could be used to bond difficult-to-join glasses. Various combinations of Pyrex, Vycor, porcelain, and soft glass were joined by placing a piece of the plumbite-treated cotton fabric between the two pieces to be joined and heating the assembly to a temperature of 600°C (Fig. 4). The time required at this temperature varied somewhat with the rate of heating and the size of the objects to be bonded, but was usually of the order of 1 hr. After cooling, the bond was so strong that the joined glasses ruptured more readily than the bond itself. This can be seen in Figure 4B, where part of the porcelain broke, rather than the bond. Cotton fabrics with lead contents varying from 8% to 20% performed equally well as adhesives.

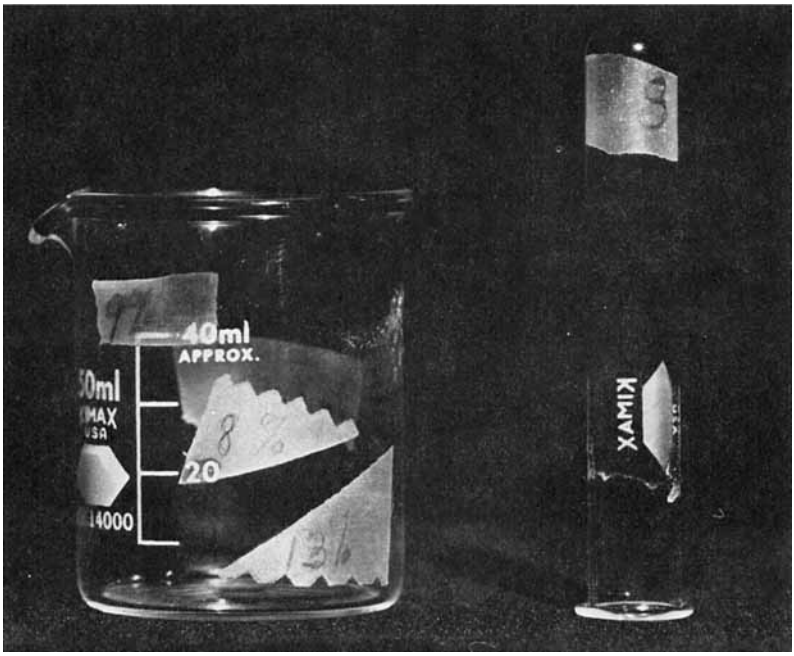

Fig. 2. Pencil labels using cotton print cloth having different lead contents. Lead content on label.

When the glassy flakes are lifted from the original glass substrate, there remains at the interface an etched surface of the same shape and weave pattern as the fabric used (Fig. 5).

Other amphoteric elements such as tin, aluminum, and copper were applied to cotton cellulose under basic conditions in a manner analogous to that used with plumbite. None was taken up by cotton as easily as was the plumbite, and no glass formed from the cottons that had been treated with salts other than the plumbite.

All high-silicate glasses served well as sources of silicon or substrates for the new glassy materials. Soft glass distorted somewhat from the heat and produced a less transparent new glassy product than did Pyrex, Kimax, Vycor, porcelain, or similar high-temperature glasses.

Sand, silicon dioxide, sintered silicon, silicic acid, water glass, calcium silicate, and Dow Corning silicone vacuum grease were all tried as the source of silicon. Only the silicone grease acted as a source of silicon, and the product was completely different from that produced when glass was used. When plumbite-treated fabric was smeared with Dow Corning silicone grease and heated under the same conditions as for glass, an eggshell-type product resulted. The product was white, opaque, and fragile. It maintained the fabric shape, but the weave pattern was not detectable. Silicon-to-oxygen bonding in a silicone resembles that of glasses more than that of the other materials tested.

Since formation of new materials seemed to begin at the interface between plumbite-treated cellulose and glass substrate, thicker fabrics or mats were tested to see if they would produce thicker sheets of new glassy material.

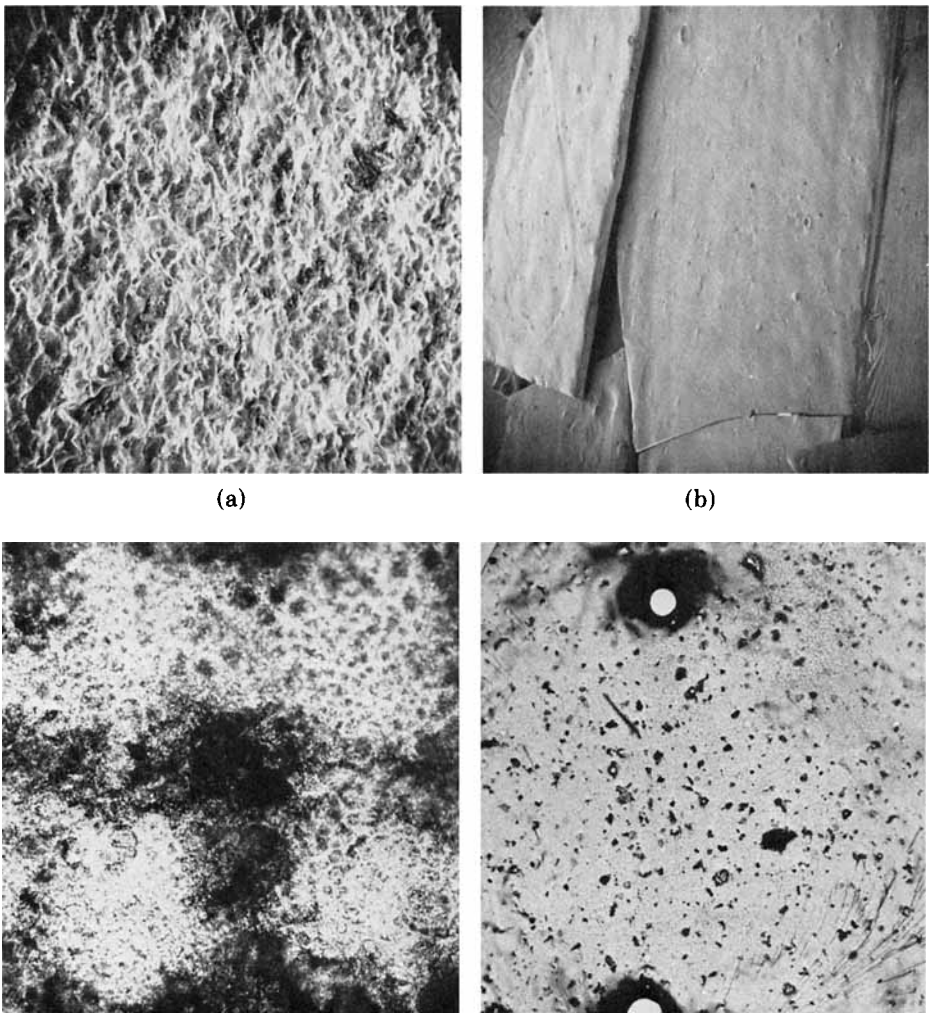

Fig. 3. Electron micrographs of glassy materials made by heating plumbite-treated cotton on Pyrex-type glass: (a) low magnification, 8% lead; (b) low magnification, 37% lead; (c) high magnification, 8% lead; (d) high magnification, 37% lead.

The thickness of product from one layer of 80 × 80 cotton printcloth varied from 0.005 to 0.013 in. A double layer resulted in a glassy product 0.008 in. thick. A 1/16-in.-thick fabric mat produced an irregular surface having thicknesses within the range of variability shown by a single layer of printcloth. Thicker glassy products were not formed by use of thicker pads of treated cellulose.

Lead oxide alone did not produce the glassy new material. When lead monoxide was heated using the same conditions of temperature and time as in making the glassy materials from treated fabric, a glassy material was formed, but one that was soft, yellow, and susceptible to chemical attack. When equal parts of finely divided carbon and lead monoxide were physically mixed, a glassy material was also formed which did not resemble that pro-

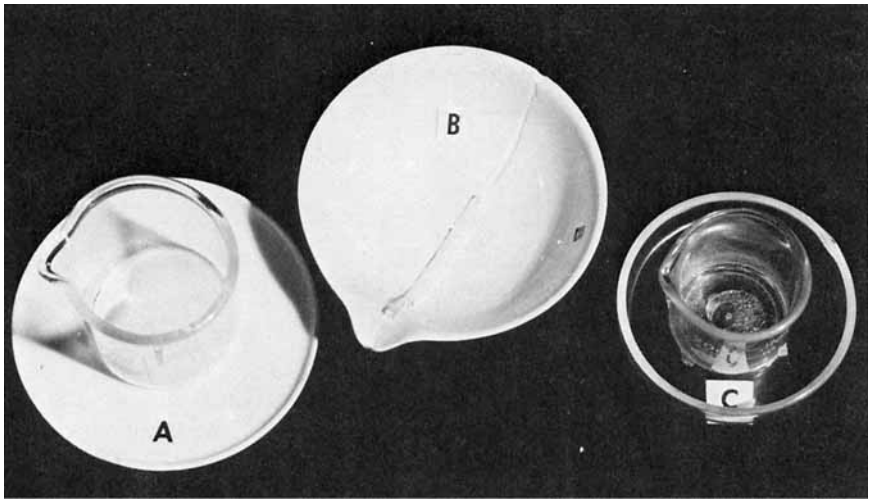

Fig. 4. Plumbite-treated cotton as bonding agent: (A) Pyrex to porcelain; (B) soft glass to porcelain; (C) Pyrex to Pyrex.

duced from the treated fabric; in this case, the loss of weight after heating indicates that all of the carbon had been lost.

Data obtained by ESCA of the glassy materials prepared from cotton fabrics with different levels of lead content are presented in Table I. The ratios of silicon to oxygen and of lead to carbon are similar in both products. This suggests that similar bonds between silicon and oxygen and between lead and carbon exist in the two structures. The greater ratio of carbon to silicon in the label made from the low lead-content cotton fabric explains the obvious

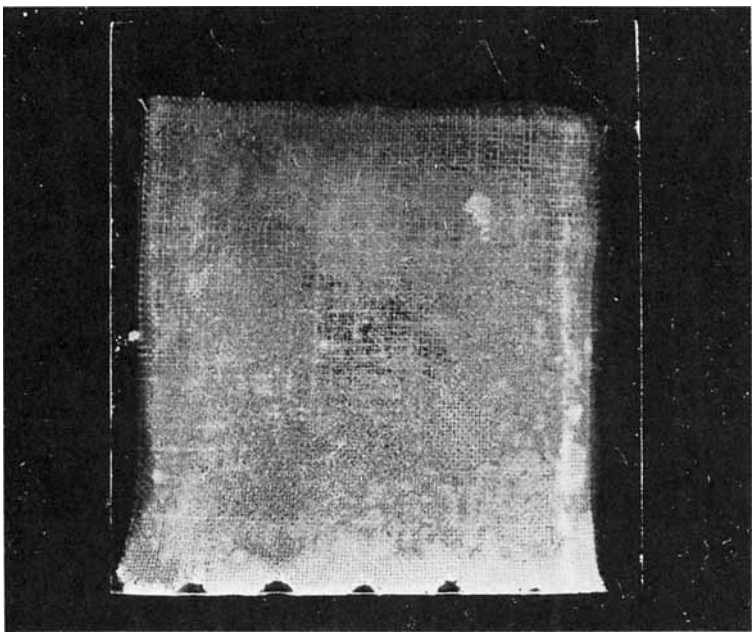

Fig. 5. Etched surface of soft glass after removing flakes of new glassy material.

TABLE I
ESCA Analysis of Glassy Materials

	Wt, %		g atoms/100 g		Atom ratio element/Si	
	A[a]	B[b]	A[a]	B[b]	A[a]	B[b]
O	16.97	48.6	1.06	3.04	9	10.5
C	16.97	13.1	1.41	1.1	12	3.8
Si	3.32	8.4	0.12	0.3	1	1
Pb	62.73	30.0	0.30	0.145	2.5	0.5

[a] Glassy label made from cotton containing 8% lead.
[b] Glassy flakes made from cotton containing 37% lead.

fabric weave pattern left in the label. If excess carbon is acting as a filler, this would explain the more translucent appearance of the label, since fillers cause opacity by scattering light at the additional interfaces.[5] By contrast, the glassy material made from the high lead-content fabric had less carbon left compared to silicon, resulting in less obvious weave pattern (Fig. 1) and greater transparency.

Thermogravimetric analyses of reactants as glassy products were formed during heating in a 10% oxygen–90% nitrogen atmosphere showed that all weight losses had occurred before the temperature reached 500°C. This indicates the carbon remaining in the new glassy materials when they are formed is retained to a temperature of 1200°C.

The new glassy materials were colorless when formed. The flame of a Bunsen-type burner applied directly to the surface of these materials caused gold color to develop. Continued application of flame resulted in a grey, silvery color. The color could be removed by either reheating the sample in an oven to about 600°C or applying the Bunsen-type flame to the reverse side of the glassy material.

Since direct flame of the burner was a reducing atmosphere and conditions that removed the color were oxidizing, it was reasoned that the color was produced by reduction of lead to the metallic state. ESCA and electrical resistivity measurements showed that the colored surface was not metallic. The colored surface was shown by ESCA to be of the same elemental composition and to contain lead in the same oxidation state as the original colorless material. The surface, after heating, was not electrically conductive, indicating that the color was not due to metallic lead. The color change could not be induced by exposure to radiation of cobalt 60 for 3 hr or uv radiation at 3500 Å or 2537 Å for 6 hr, indicating that the color change is not an F-center effect. The color may have been due either to particle size or ordering of the lattice structure. Incoherent scattering of x-rays by the lead atoms precluded use of x-ray diffraction to determine lattice structure.

SUMMARY

The preparation and products are not usual for either glasses or polymers, but are related to both. Silicon-to-oxygen bonds and carbon-to-oxygen bonds are very similar in length and energy. The silicon–oxygen–silicon bond is very flexible (angle 104° to 180°). This flexibility may allow for in-

clusion of both carbon and lead into the matrix of the new glassy material in a manner similar to the way it participates in formation and properties of siloxanes.[5]

A proposed explanation of the mechanism for formation of the new glassy materials is as follows:

1. The cotton fabric containing lead is heated, causing cellulose to be carbonized and leaving a skeleton of lead, oxygen, and carbon having the same weave pattern and fabric shape as the starting fabric. The ratio of carbon to lead becomes fixed at about six carbon atoms per lead atom. Excess carbon goes off as CO_2. The plumbite has previously been shown by x-ray diffraction to be uniformly distributed throughout the fabric structure,[1] and it remains uniformly distributed in the carbon skeleton.

2. Continued heating results in the disruption of silicon-to-oxygen bonds in the surface of the original substrate (glass or porcelain holder) and permits silicon atoms to migrate into a lead–oxygen–carbon polymeric skeleton and form new bonds. The ratio of silicon-to-oxygen atoms in the glassy product becomes fixed at about ten oxygen atoms per silicon atom. Lead attracts silicon from the substrate. The lead is present as some form of oxide, and metal oxides have been used as catalysts in polymer formation.[5] The fabric with 37% lead attracts enough silicon to produce a glassy material with two silicon atoms per lead atom, whereas the fabric with only 8% lead attracts only enough silicon to form a glassy material with 0.4 silicon atom per lead atom. The more lead that is present, the more silicon atoms are pulled out of the surface of the substrate and the more likely is a fracture at the interface upon cooling. This would explain why higher lead contents of fabric yield products that can be separated from the substrate. Also, since a smaller proportion of silicon atoms is taken into the matrix when the lead content of the fabric is low, the resultant product has more of the lead–oxygen–carbon skeleton which is retained as weave pattern or fabric design. The structure is amorphous, which imparts glass-like properties and makes the materials nonconductive.

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References

1. T. L. Ward and R. R. Benerito, *Text. Res. J.*, **44**, 12 (1974).
2. R. C. Griffin, *Technical Methods of Analysis*, McGraw-Hill, New York, 1927, pp. 235.
3. R. T. O'Connor, *Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose*, Vol. 3, Marcel Dekker, New York, 1972, pp. 8–16, 46–50, 183–185, 314–320, 30–32.
4. C. C. Klick, *American Institute of Physics Handbook*, 2nd ed., D. E. Gray, Ed., McGraw-Hill, New York, 1963, Sect. 9, pp. 123–127.
5. Ferdinand Rodriguez, *Principles of Polymer Systems*, McGraw-Hill, New York, 1970, pp. 247, 12, 62.

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