

Ultraviolet Curing Acrylated Chlorinated Low-Molecular-Weight Guayule Rubber Wood Filler and Finish

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SYNOPSIS

Acrylated chlorinated low-molecular-weight guayule rubber (ACLMWGR) has been synthesized and characterized with Fourier transform infrared spectroscopy, solid-state nuclear magnetic resonance spectroscopy, and differential scanning calorimetry. We have found that ACLMWGR is useful as a prepolymer in 100% solids ultraviolet (UV) curing wood coatings. The properties of the coatings are equal or superior to coatings prepared from acrylated chlorinated rubber synthesized from commercial masticated natural rubber. However, when low-molecular-weight guayule rubber (LMWGR) serves as the feedstock, the cost of producing ACLMWGR is significantly reduced since no mastication is needed.

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INTRODUCTION

Guayule (*Parthenium Argentatum* Gray), a shrub growing in southwestern Texas and northern Mexico, is considered promising as a source of domestic rubber with qualities equal or superior to hevea rubber (Malaysian rubber).¹ Low-molecular-weight guayule rubber (LMWGR) is one of the four major co-products in the guayule rubber extraction process.² In order to offset the cost of planting, cultivation, harvest, and extraction, commercialization of all the co-products is highly desirable. Our present efforts have focused on commercialization of the guayule co-products in surface coatings and adhesives.²⁻⁷ Specifically, we have synthesized and characterized a variety of useful co-product derivatives of LMWGR including chlorinated rubber,³ chlorinated hydroxyrubber,⁴ cyclized rubber,⁵ epoxidized rubber,⁶ maleinized rubber, and chlorinated maleinized rubber.⁷

Chlorinated rubber has long been a staple in the manufacture of organic coatings. It provides such properties as excellent chemical and water resistance, excellent durability, and good flame retardancy. Accordingly, it has been our objective to confirm that LMWGR offers coating properties equal

or superior to commercial chlorinated rubber produced from synthetic rubber or masticated hevea rubber.^{2,3} However, the conventional applications of chlorinated rubber are limited to solvent-based coatings containing high volatile organic content (VOC). High VOC coatings do not comply with environmental regulations and are being replaced by environmentally friendly technologies such as waterborne, high solids, and powder coatings. In keeping with contemporary technological trends, we have developed a novel approach to the synthesis and use of acrylated chlorinated rubber and have shown it to be an effective prepolymer when used in 100% solids ultraviolet (UV) curing coatings formulations.⁴ Ultraviolet curing coatings usually consist of a prepolymer, photoinitiator, reactive diluents, and additives.⁸⁻¹¹ Accordingly, the prepolymer composition plays a major role in determining performance properties. Moreover, solubility of the prepolymer in the reactive diluent is a key requirement. When hevea or synthetic rubber is used, mastication is required to achieve the desired level of solubility. The mastication process increases the ultimate cost to the consumer. Thus, if mastication can be avoided, the process economics are improved. In the present instance, LMWGR is used as is and no mastication is required. Herein we report the synthesis and characterization of acrylated chlorinated LMWGR (ACLMWGR). Coatings containing no

solvents (100% solids) have been formulated, cure conditions have been established, and their properties evaluated.

EXPERIMENTAL

Materials

Crude LMWGR, mixed with organic soluble guayule resin, was supplied by Bridgestone/Firestone Inc. Trichloroacetic acid, sodium methoxide (95%), acryloyl chloride, and anhydrous toluene were purchased from Aldrich. Triethylamine was supplied by BASF. Reagent-grade acetic acid was provided by Baker. Reagent-grade methylene chloride, chloroform, and methanol were obtained from Fisher Chemical. The source of the solvents and additives of the coating formulations are included in Tables III and IV.

Purification of LMWGR

The organic soluble resin contained in crude LMWGR was removed by extraction with acetone. LMWGR was twice purified by dissolving in carbon tetrachloride and precipitating from 95% ethanol.

Hydroxylated LMWGR

Trichloroacetic acid (56.8 g) was added to 350 mL 5% LMWGR in anhydrous toluene in a 500 mL Erlenmeyer flask. The solution was stirred for 23 h at 0°C under nitrogen flow after which it was transferred to a 1000 mL Erlenmeyer flask containing 60.7 g of sodium methoxide and 100 mL of methanol. After stirring for 20 h, the mixture was neutralized by 34.7 mL of acetic acid and stirring was resumed for another 15 min after which the flask contents were poured into 650 mL of methanol in an Erlenmeyer flask, and the pH of the mixture was adjusted to 5–6 with a few drops of acetic acid. The polymer was precipitated, washed with methanol and 50% (v/v) methanol in water, respectively, and dried in a vacuum oven. The hydroxylated rubber was further purified by dissolving in 100 mL of methylene chloride and precipitating from 400 mL methanol.

Chlorinated Hydroxylated LMWGR

A solution of 5% hydroxylated LMWGR (280 mL) in CHCl_3 was added to a three-neck flask fitted with a water condenser, a gas inlet tube, and a glass stopper. The inlet tube was connected via Teflon tubes to a chlorine cylinder through a gas trap. The exit port of the condenser was connected to two concen-

trated sodium hydroxide traps. The reaction flask was immersed in an oil bath for temperature control. The system was purged with nitrogen for at least 15 min before chlorine gas addition began through a gas dispersion tube. The solution was allowed to reflux with constant stirring via a magnetic stirrer. A slight excess of chlorine was added with liberated hydrogen chloride being trapped in the sodium hydroxide solutions. The product was precipitated with 600 mL of methanol after the reaction was complete.

ACLMWGR

A solution of 11.0 g of chlorinated hydroxylated LMWGR in 150 mL anhydrous toluene in a 500-mL three-neck flask equipped with a nitrogen inlet tube, a water condenser, and a dropping funnel, received the addition of 2.178 g of acryloyl chloride, and the mixture was stirred at 70°C under N_2 flow. A solution of 2.450 g of triethylamine in 50 mL of anhydrous toluene was added dropwise over 1 h, and the reaction was continued for an additional 2 h. The white but yellow tone product was precipitated from 800 mL of methanol, dried, and further purified by dissolving in methylene chloride and precipitating from methanol.

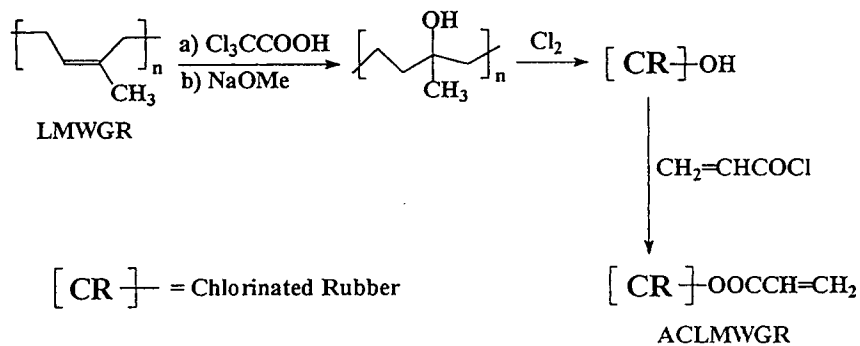
Characterization Methods

Samples were dissolved in deuterated chloroform at 2–3% (w/v) and a Bruker model AC-200, 200 MHz NMR spectrometer was employed for semiquantitative nuclear magnetic resonance (NMR) spectroscopy measurements. Peak integrations of well-resolved spectra were used for calculations of percent hydroxylation using Eq. (1). Samples for Fourier transfer infrared (FTIR) spectra were cast onto sodium chloride plates in methylene chloride and solvent removed *in vacuo* at < 0.5 mm Hg and approximately 25°C for at least 2 h. FTIR spectra were then recorded (64 scans for a resolution of 2 cm^{-1}) on a Perkin-Elmer model 1600 FTIR spectrophotometer. Differential scanning calorimetry (DSC) analysis was performed on a Mettler TA4000 system using a heating rate of 10°C/min. Elemental analyses were performed by M-H-W Laboratories.

COATING FORMULATIONS AND PERFORMANCE TESTS

Wood Filler

Pigment, additives, photoinitiators, ACLMWGR, and the reactive diluents were combined and dis-



Scheme 1 Synthetic route of ACLMWGR.

persed at 1500 rpm with a high-speed disperser for 1 h to a Hegman 7.5 grind. The coatings were applied on sanded maple wood with a draw bar at a wet thickness of 2 mils. The coated samples were cured with a 450-W medium pressure mercury UV lamp for 4 min at an 11-cm distance.

Wood Finish

Photoinitiators, additives, and ACLMWGR were dissolved in the acrylate mixture. The coatings were applied by draw bar at 1 wet mil on sanded but filled maple panels. The coatings were irradiated for 4 min under identical conditions used for the filler coat.

Tests

Maple wood panels (Hillyard) were used for all tests except when polyethylene panels were used to prepare samples for tensile strength and elongation measurements. All evaluative tests were conducted according to standard methods (Tables III and IV). Tensile strength/elongation measurements were performed with an Instron Testing Machine (Model A1020C, Instron Corp.). The thickness of the tensile test samples was measured with a caliper of 0.0001 in. sensitivity. The viscosity of the coating was determined by a Brookfield model DV-II digital viscometer fitted with a #31 spindle at speeds of 1.5–6 rpm.

RESULTS AND DISCUSSION

Synthesis and Characterization

ACLMWGR was synthesized (Scheme 1) via acrylation of chlorinated hydroxylated LMWGR with triethylamine as catalyst. The synthesis and characterization of chlorinated hydroxylated LMWGR

were reported previously⁴ as being prepared by the chlorination of partially hydroxylated LMWGR, the latter being obtained from the saponification of the addition product of LMWGR and trichloroacetic acid.^{4,12} A typical ¹H-NMR spectrum of hydroxylated LMWGR is shown in Figure 1. In addition to three major polyisoprene absorptions (δ 5.13, 2.04, and 1.68 ppm, corresponding to vinyl, double-bond methylene, and double-bond methyl protons, respectively), two additional absorptions corresponding to methyl protons (δ 1.16 ppm) and methylene protons (δ 1.42 ppm) are prominent. The fraction of hydroxylated isoprene units (F) can be calculated from the integration areas of the corresponding methyl proton absorption (1.16 ppm) and double-bond methyl proton absorption (1.68 ppm) in the NMR spectrum.⁴ The hydroxyl content of the chlorinated hydroxylated LMWGR (H_C) can be calculated from F and chlorination content (C).

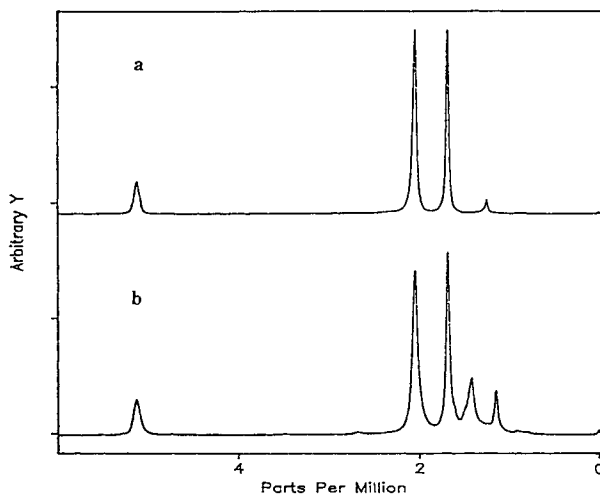


Figure 1 Typical ¹H-NMR spectra of (a) LMWGR and (b) hydroxylated LMWGR.

Table I Properties of Chlorinated Hydroxylated LMWGR (CHLMWGR)

	CHLMWGR	(CHR ^{4,15}) ^a
Hydroxyl content (Wt)	1.8%	(1.5%)
Chlorine content (Wt)	48.3%	(49.4%)

^a Values for chlorinated hydroxylated rubber (CHR) are added for comparison.

$$H_C = (1 - C)F \quad (1)$$

Accordingly, the properties of chlorinated hydroxylated LMWGR are tabulated in Table I.

The acrylate content (AC) of ACLMWGR was calculated from the H_C of chlorinated hydroxylated LMWGR based on complete conversion as evidenced by FTIR spectroscopy.

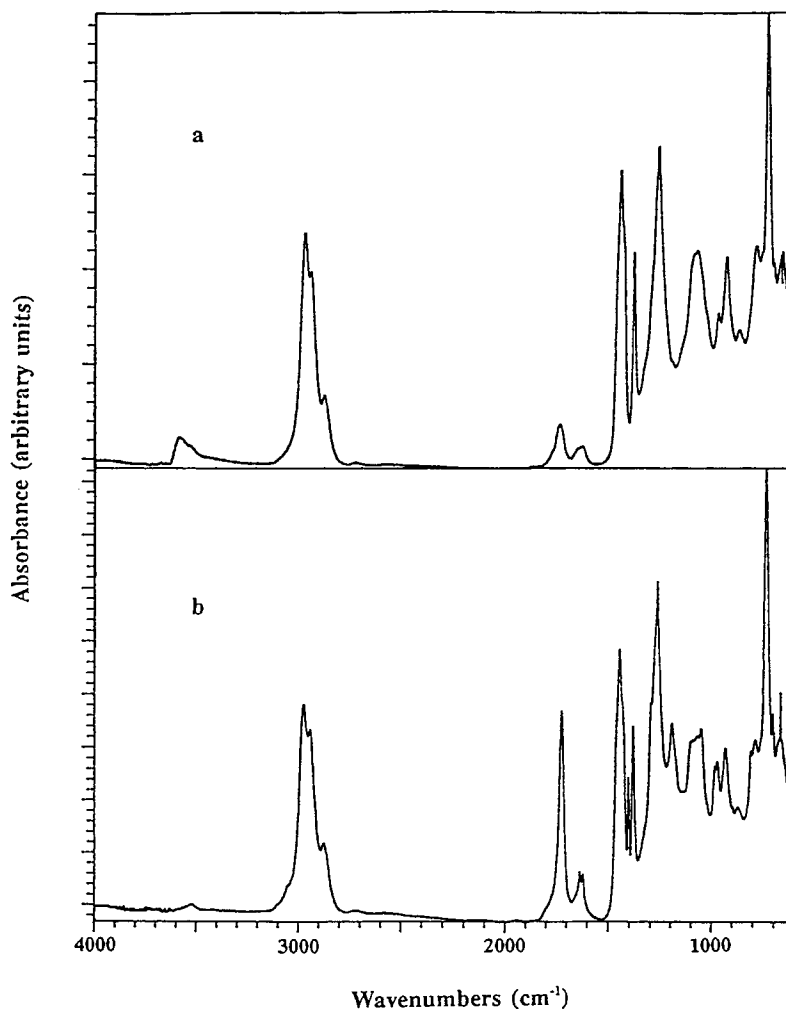
Table II Properties of ACLMWGR

	ACLMWGR	(ACR ^{4,15}) ^a
Chlorine content (Wt)	46.4%	(46.5%)
Acryl content (Wt)	7.0%	(6.8%)
T_g (°C)	77.9	(83.9)

^a Values for acrylated chlorinated rubber (ACR) are added for comparison.

$$AC = \frac{H_C (71/17)}{1 + H_C (71/17 - 1)} \quad (2)$$

The properties of ACLMWGR are listed in Table II. The FTIR spectra of chlorinated hydroxyrubber and acrylated chlorinated rubber are shown in Figure 2(a) and 2(b), respectively. The absorption corresponding to the hydroxyl stretching vibration fre-

**Figure 2** FTIR spectra of (a) chlorinated hydroxylated LMWGR and (b) ACLMWGR.

quency ($3400\text{--}3600\text{ cm}^{-1}$) in Figure 2(a) disappeared completely according to Figure 2(b). The presence of acrylate is evidenced by the characteristic absorptions ($1719, 1635, 1403, \text{ and } 1198\text{ cm}^{-1}$) in Figure 2(b).¹³ In both, the absorption corresponding to C—Cl bond vibrational frequency (758 cm^{-1}) is dominant.

The ^{13}C -NMR spectra of chlorinated hydroxy-rubber and ACLMWGR are shown in Figures 3(a) and 3(b), respectively. The spectroscopic pattern below 80 ppm of Figure 3(b) is very similar to that of Figure 3(a), and the broad nature of the absorptions from 20 to 80 ppm confirm the structural complexity of the product. Makani and co-workers¹⁴ have attributed the broad absorptions from 18 to 59 ppm to methyl carbon ($-\text{CH}_3$), methylene carbon ($-\text{CH}_2-$), and the methyl carbon linked to a single chlorine ($-\text{CH}_2\text{Cl}$) contributions, respectively. The broad 66-ppm absorption was attributed to the methylene carbon bond holding a single chlorine ($-\text{CHCl}-$). The 75 ppm absorption is attributable to the tertiary carbon bonded to a single chlo-

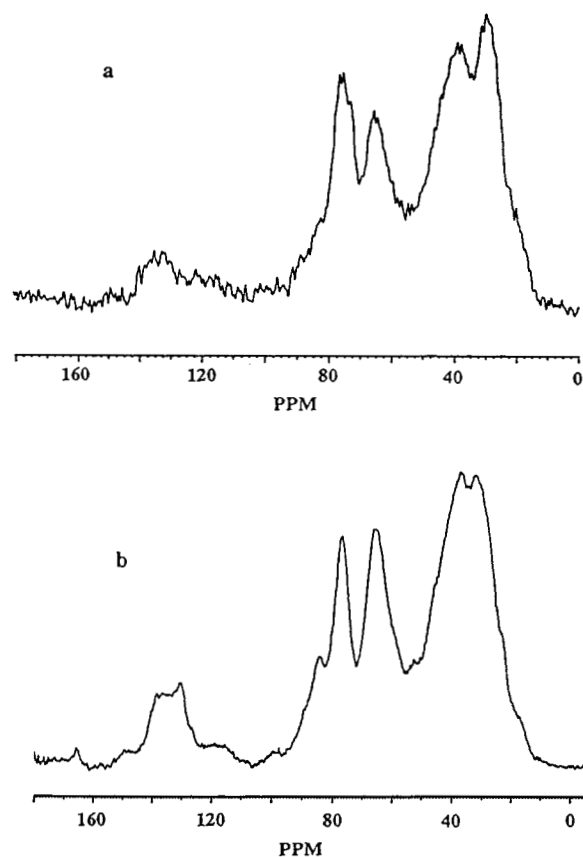


Figure 3 ^{13}C -NMR spectra of (a) chlorinated hydroxylated LMWGR and (b) ACLMWGR.

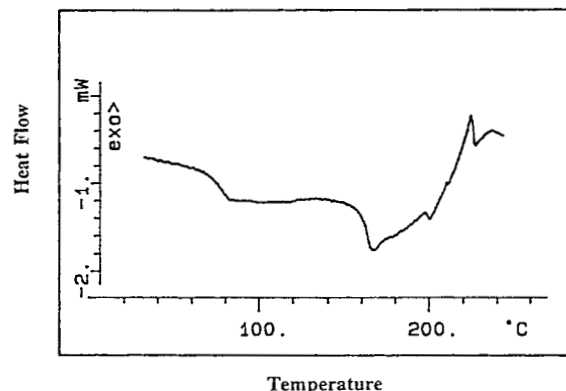


Figure 4 Typical DSC thermogram of ACLMWGR.

rine ($\text{>CCl}-$, $74\text{--}77\text{ ppm}$)¹⁴ contribution. In the case of chlorinated hydroxylated LMWGR [Fig. 3(a)], the tertiary carbon attached to the hydroxyl moiety is likewise a contributor to the 75 ppm absorption. A number of the new absorptions appear in the chemical shift region above 80 ppm for ACLMWGR [Fig. 3(b)]. The broad 131 ppm absorption is a result of the remaining vinyl double bonds of the chlorinated rubber as well as the acrylic carbon-carbon double bonds. The weak 165 ppm absorption indicates the carbonyl presence.

Thus, while the spectroscopic analyses confirm the success of the chlorination and acrylation, the structural determination of chlorinated rubber derivatives is difficult and the exact structure of ACLMWGR remains unknown.^{4,14}

Thermal Properties

The glass transition temperature of ACLMWGR (Fig. 4) was measured as 77.9°C . Its thermal behavior above 150°C is complex and includes the endothermic decomposition of the C—Cl bond, the melting point, and an exotherm attributed to reaction of the acrylate functionality.

UV Curing Wood Filler and Finish

ACLMWGR was used for both the filler coat and clear wood finishes. Extender pigments were incorporated into the filler formulation to reduce cost and to enhance the sanding properties. Acrylate monomers were used as reactive diluents. The combination of photoinitiators of the cleavage (Irgacure 651) and abstraction types (benzophenone) enhanced the curing efficiency.

Hardness and flexibility of the coatings can be adjusted by careful selection of the reactive diluents where increasing amounts of trifunctional diluents (e.g., Photomer 4094 and Photomer 4149 from Henkel) give increases in crosslinking density and a concomitant property move toward brittleness. The formulation examples are listed in Tables III and IV. The UV-cured fillers (Table III) show excellent adhesion, good chemical, water and solvent resistance, and excellent sanding properties.

The UV-cured finishes (Table IV) are attractive, smooth, hard, and of high gloss. The coatings are further characterized by excellent adhesion and good water, chemical, and solvent resistance. For instance, neither shows any effect after 500 methyl ethyl ketone (MEK) double rubs.

Table III Matte UV Curing Acrylated Chlorinated ACLMWGR Wood Filler

Material	Amount (g)	Suppliers
ACLMWGR (ACR ^{4,15})	15.8 (15.8)	USM
Photomer 4061	50.0	Henkel
Photomer 4094	20.0	Henkel
Photomer 4770	5.0	Henkel
Byk 065	0.7	Byk
DisperByk 163	2.5	Byk
Microwhite 50	30.0	E.C.C.
Irgacure 651	1.0	Ciba-Geigy
Benzophenone	2.0	Dainippon

Ground to Hegman 7.5 with high speed mixer at 1500 rpm for 1 h

ACLMWGR (ACR ^{4,15}) ^a	Filler Properties:	ASTM Method
Viscosity @ 25°C, cps	5300 (4460)	
Wet film thickness	2 mils (2)	
Adhesion	5B (5B)	D-3359
Pencil hardness	5 H (5H)	D-3363
Tensile strength, psi	4500 (4300)	D-2370
Elongation at break	8% (8%)	D-2370
MEK double rub	500+ (200 +)	D-4752
8 hour spot tests:		D-1308
Water	5 (5)	
Concentrated NH ₄ OH	5 (4)	
10% NaOH	5 (4)	
20% H ₂ SO ₄	5 (5)	

5 = no effect; 4 = stain only; 3 = blistering;
2 = lifted film; 1 = failure

^a Values reported for ACR filler are added for comparison.

Table IV High Gloss UV Curing ACLMWGR Wood Finishes

Material	Amount (g)	Suppliers
ACLMWGR (ACR ^{4,15}) ^a	22.0 (22.0)	USM
Photomer 4127	20.0	Henkel
Photomer 4061	20.0	Henkel
Photomer 4094	30.0	Henkel
Photomer 4149	6.0	Henkel
Photomer 4770	10.0	Henkel
Byk 065	0.7	Byk
Byk 325	1.5	Byk
Irgacure 651	2.0	Ciba-Geigy
Benzophenone	2.0	Dainippon

ACLMWGR (ACR ^{4,15}) ^a	Finish Properties:	ASTM Method
Viscosity @ 25°C, cps	3660 (2970)	
Wet film thickness	1 mil (1)	
Adhesion	5B (5B)	D-3359
Pencil Hardness	4H (4H)	D-3363
Tensile strength psi	3900 (3500)	D-2370
Elongation at break	7% (7%)	D-2370
60° gloss	85 (80)	
MEK (double rub)	500 + (200+)	D-4752
8 hour spot tests:		D-1308
Water	5 (5)	
Concentrated NH ₄ OH	4 (4)	
10% NaOH	4 (4)	
20% H ₂ SO ₄	5 (5)	

5 = no effect; 4 = stains only; 3 = blistering;
2 = lifted film; 1 = failure

^a Values reported for ACR finish are added for comparison.

Thus, UV-cured ACLMWGR coatings possess excellent properties and are certainly equal to those prepared from masticated, acrylated chlorinated hevea rubber.^{4,15}

CONCLUSIONS

Acrylated chlorinated low-molecular-weight guayule rubber has been synthesized and used as a reactive diluent in the formulation of environmentally compliant, ultraviolet curing, 100% solids wood filler, and finish coatings. The cured coatings are of a quality equal to those synthesized from masticated hevea rubber.

USDA is gratefully acknowledged for its financial support of this work (under contract #89-38200-4372). We are

particularly grateful to Drs. Daniel Kugler, Davis Clements, and Mrs. Carmela Bailey for their continued encouragement and assistance.

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Received November 10, 1993

Accepted May 10, 1994