

Grafting of Chelating Monomers to Styrene-Butadiene Latexes

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Synopsis

It has been previously reported that vinyl esters have been grafted to natural rubber latex. We have grafted two other types of vinyl monomers to styrene-butadiene latex. These monomers are the ammonium salts of acrylic acid and methacrylic acid, and the ammonium salts of vinyl chelating agents, such as *N*-(*ar*-vinylbenzyl)iminodiacetic acid. (Ionizing radiation doses of 0.5-2 Mrad are sufficient to accomplish the grafting.) These monomers, in the range of 2-6%, give very definite improvement in adhesion to metals. They also improve the rust resistance, and when pigmented with an iron oxide dispersion, improve the whitening resistance of the coating. The vinyl chelating monomers give the best improvement over the untreated latex, particularly in the resistance to whitening. The optimum amount of monomer is 4-6%. This compares very well with the theoretical amount for a monomolecular layer of monomer surrounding each latex particle.

INTRODUCTION

Considerable work has been done on grafting vinyl monomers to latex polymers. Oster and Shibata¹ have grafted acrylamide to natural rubber latex. Menon and Kapur² have grafted methyl methacrylate to natural rubber latex. Ultraviolet light was used as the initiator in both cases. Vinyl esters have also been grafted to latexes with the use of ionizing radiation as the initiator.³ Most of this work was directed toward improving the physical properties of the latex films, especially water resistance, flexibility, and impact strength. Chelating agents, when combined with a coating material, should improve the adhesion of the coating to the metal surface. However, it has been observed that the addition of certain chelating agents such as pentanedione or Versene 100 actually increases the corrosion of the metal,³ rather than inhibiting the corrosion. Small chelating agents such as these are able to work behind surface molecules and pull the metal ions or oxide molecules away, intensifying corrosion. With large chelating agents, especially polymeric ones, this should not occur. Instead, the large molecules might be attracted across several surface molecules to prevent their being pulled off, further corrosion thereby being inhibited. Theoretically, the method which would produce the best metal coating would be that of joining the coating with the metal surface chemically as well as physically. One procedure for approaching this

would be to graft a vinyl chelating agent to the polymeric latex particles. Then when the grafted latex is applied to the metal, chelation would chemically unite the coating and the metal. This should produce a superior coating which could find application in primer paints. Styrene-butadiene latexes would be desirable in primer formulations because of their economy, nontoxicity, nonflammability, and ease of application.

EXPERIMENTAL

Four chelating monomers were used in this study. Polymers and copolymers of these have been shown to exhibit chelating properties.⁴ These monomers are: *N*-(*ar*-vinylbenzyl)iminodiacetic acid, *N*-(*ar*-vinylbenzyl)-aspartic acid, *N,N*-bis(*ar*-vinylbenzyl)glycine, and 2-(vinylphenyl)glycine. Two other monomers were studied along with these: ammonium acrylate and ammonium methacrylate. These are not chelating agents, but act similarly, and tend to aid in producing a better metal coating. They are not as effective as the chelating monomers, as will be shown, but definitely give improved adhesion.

All of the latexes used in the study are styrene-butadiene latexes produced by the Dow Chemical Co. The metal panels used in these experiments were bonderized steel purchased from Parker Rust-Proof Co., Detroit. The radiation source used was a 1-M.e.v. electron beam generator (General Electric resonant transformer). The latex was pumped through a pipe having a 0.004 in. titanium window to allow maximum penetration of the 1-M.e.v. electrons. The vinyl chelating monomer solution was added and mixture was stirred well. Grafting took place in

TABLE I

	Grade	Definition
Adhesion	Grade 1	Coating unchanged; coating cannot be scraped from panel without removing metal
	Grade 2	No visible change; coating may be scraped off with knife
	Grade 3	Trace of tiny blisters; coating can be peeled from panel
	Grade 4	Small blisters or peeling
	Grade 5	Large blisters or peeled sections
Rust resistance	Grade 1	Coating unchanged; no trace of corrosion
	Grade 2	Coating may show only traces of corrosion in limited quantities
	Grade 3	Slight corrosion in small areas
	Grade 4	Noticeable corrosion in large areas
	Grade 5	Large part of panel rusted severely
Resistance to whitening	Grade 1	Coating unchanged; no water line visible
	Grade 2	Color is unchanged except at water line
	Grade 3	Water line is definite and coating is lighter in some areas
	Grade 4	Entire coating is noticeably lighter below the water line
	Grade 5	Entire coating is a light pink to white below water line

4–10 hr. This was accelerated to less than 1 hr. by heating the mixture at 50°C.

The dose rate was varied by changing the beam current of the 1-M.e.v. electron beam tube. It can be varied from a few microamperes to 5 ma. The total dose was varied by changing the flow rate of the latex under the electron beam. The monomers were added immediately after irradiation and the mixtures were stored over night at room temperature.

After the grafting was completed, the latex was pigmented with an iron oxide automotive primer pigment dispersion. The pigmented latex was applied to the metal panels by the use of a Meyer wire wound rod. After drying 1 hr., the panels were baked 30 min. at 300°F. Then panels were placed in a 95°F. water bath for 300 hr. At the end of the 300 hr., the panels were removed, dried, and evaluated for whitening, rusting, and blistering.

The panels were graded by visual comparison. The grades used are listed in Table I.

RESULTS AND DISCUSSION

Evidence of Grafting

In order to show first that vinyl monomers may be grafted to latex polymers, we prepared a series of samples in the following manner. A sample of styrene-butadiene latex was given a dose of 2 Mrad with 1 M.e.v. electrons. To 100 g. of this, we added 5 ml. of a 20% solution of ammonium acrylate (this is equivalent to 2% based on solids). To another 100 g. portion, we added 10 ml. of ammonium acrylate (4% based on solids). Similarly, to some unirradiated latex, the monomers were added. These were allowed to stand at 25°C. for 24 hr. for grafting to take place. Films were cast from these four latex samples and also from irradiated latex with no monomer added, and from unirradiated latex with no monomer added. These films were vacuum dried, then analyzed by infrared spectroscopy for carbonyl bands. Only the first two films (irradiated, monomers added) showed a change in the 5.75 μ band (*B* and *C*, respectively, in Fig. 1). The bands at 5.1, 5.3, 5.5, and 5.75 μ are overtones from a monosubstituted aromatic ring. The carbonyl band appears at 5.8 μ and causes the 5.75 μ band to be shifted or blacked out. All other films were essentially identical (*A* in Fig. 1). One might expect the ammonium acrylate to remain in the unirradiated latex film since the monomer is a solid. But when it is put in solution, it decomposes to give ammonia and acrylic acid. The ammonia is liberated in the drying process, driving the equilibrium to yield more acrylic acid. After all of the ammonia is evaporated, the acrylic acid also evaporates as the film dries. An 18% aqueous solution of ammonium acrylate monomer was evaporated to dryness. No monomer remained. Only a trace of poly(acrylic acid) remained. Since the latex was irradiated before the monomer was added, we assume that most of the polymerization occurred as grafting and little or no homopolymerization took place.

This series of experiments was further amplified by taking portions of the four latexes mentioned above, that is, (I) irradiated latex + monomer (4% ammonium acrylate); (II) unirradiated latex + monomer (4% ammonium acrylate); (III) irradiated latex; and (IV) unirradiated latex, then adding an iron oxide pigment dispersion. When these were applied to metal panels, III and IV were identical, both showing subsurface corrosion in the form of small fish-eyes or spots in the coating. Latexes I and II appeared to be about equal, with no subsurface corrosion. As the films dried, however,

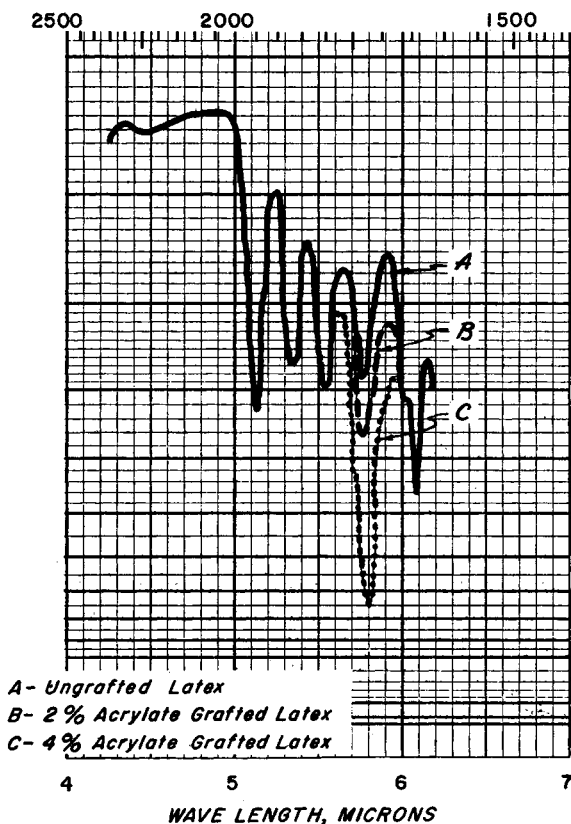


Fig. 1. Infrared analysis of latexes.

small spots began to appear in the coating made from II. The panels were then baked 30 min. at 300°F. More corrosion appeared in II, but none in I. The panels were then placed in a 95°F. water bath for 300 hr. At the end of the test period the panels were graded for adhesion, rust resistance, and whitening resistance. The results are shown in Table II. There was essentially no difference in II, III, and IV.

The same type of experiment was conducted with *N*-(*ar*-vinylbenzyl)-iminodiacetic acid, ammonium salt. The infrared comparisons could not be used since the ionized monomer is not volatile, but comparisons of

TABLE II
Ammonium Acrylate-Grafted Latex

Latex	Adhesion	Rust resistance	Whitening resistance
I	Grade 1	Grade 2	Grade 3
II	" 4	" 5	" 5
III	" 4	" 5	" 5
IV	" 4	" 5	" 5

TABLE III
Chelate-Grafted Latex

Latex	Adhesion	Rust resistance	Whitening resistance
I	Grade 1	Grade 1	Grade 1
II	" 4	" 5	" 5
III	" 4	" 5	" 5
IV	" 4	" 5	" 5

metal panels coated with pigmented latexes were made. The results of the study are shown in Table III. This is after 300 hr. in a 95°F. water bath.

Latex II resembled Latex I when the panels were prepared, even after baking. When the panels were placed in the water bath, however, the coating began to deteriorate, indicating that possibly the unpolymerized monomer in II began to be leached out. Since this did not occur in I, this is taken as evidence of grafting. Since the radiation technique used was preirradiation, rather than mutual, we assume that most polymerization occurred as grafting and little or no homopolymer was formed. Brief comparisons were made between coatings prepared by mutual and preirradiation techniques. The results were similar, but the preirradiation method gave good results more consistently.

Effect of Radiation Dose

It was desirable to find the effective dose range. In order to determine the minimum, maximum, and optimum dose, we irradiated a series of samples and added monomers as previously described. Doses of 0.5, 1, 2, 5, and 10 Mrads were given to samples of a 60-40 styrene-butadiene latex, and 10% ammonium acrylate (based on solids) was added. These mixtures were heated to 50°C. for 2 hr. Films were cast and dried in a vacuum

TABLE IV
Effect of Radiation Dose on Grafting Ammonium Acrylate

Dose, Mrad	% Grafted
0.5	4.3
1	6.5
2	9.6
5	8.5
10	10.0

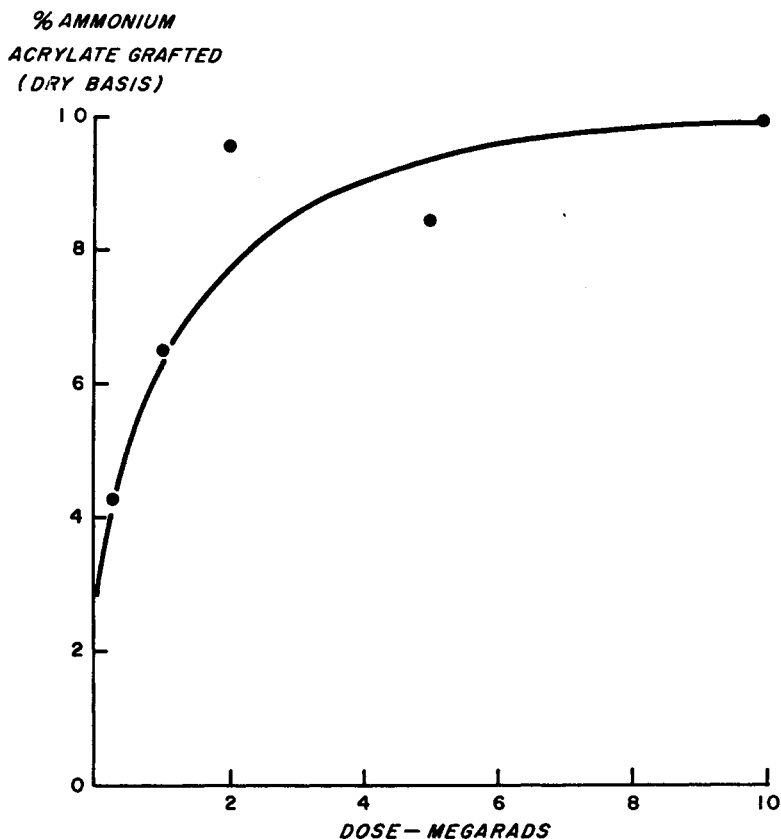


Fig. 2. Effect of radiation dose on grafting ammonium acrylate to latex.

oven at 80°C. The amount of monomer grafted was determined by infrared analysis. The results are shown in Table IV and in Figure 2.

A similar group of experiments was run with the use of *N*-(*ar*-vinylbenzyl)iminodiacetic acid, ammonium salt. In these experiments, the grafted latexes were pigmented and applied to metal panels. They were evaluated after 300 hr. in a 95°F. water bath. The results are shown in

TABLE V
Effect of Radiation Dose on
Grafting *N*-(*ar*-Vinylbenzyl)iminodiacetic Acid, Ammonium Salt

Dose, Mrad	Adhesion	Rust resistance	Whitening resistance
0	Grade 4	Grade 5	Grade 5
0.01	" 4	" 4	" 4
0.1	" 3	" 2	" 2
1	" 1	" 1	" 1
5	" 1	" 1	" 1
10	" 1	" 1	" 1

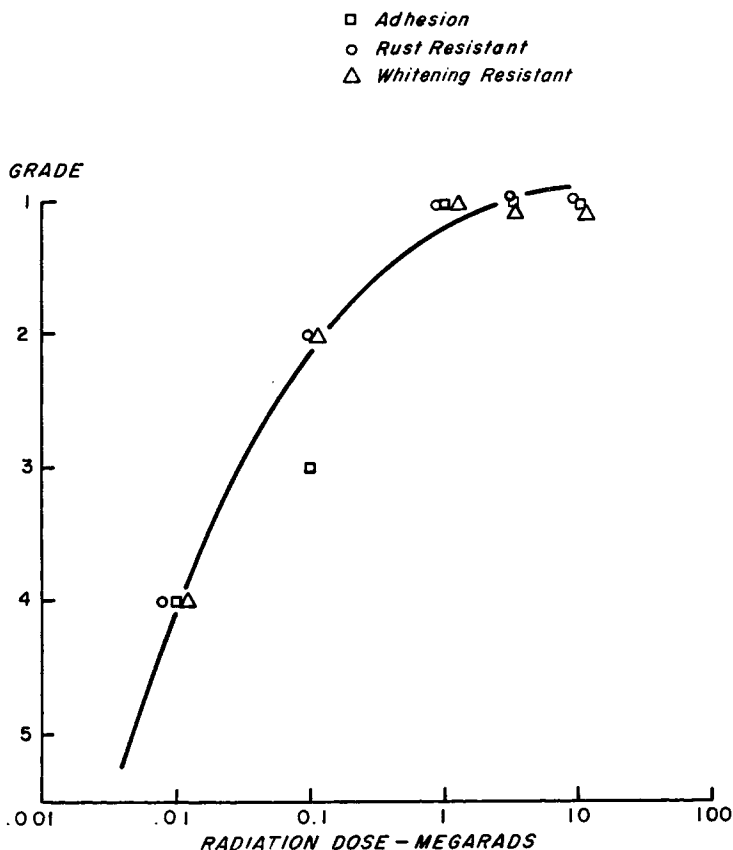


Fig. 3. Effect of radiation dose on physical improvement of latex.

Table V and Figure 3. A dose of 0.1 Mrad is sufficient for a noticeable improvement, but 1 Mrad appears to be more desirable. Going above 1 Mrad does not give further improvement, and does not appear to be detrimental.

Effect of Dose Rate

A series of samples was irradiated at different dose rates by changing the current of the electron beam generator from 0.1 ma. to 5 ma. Each sample was given the same total dose, and an equal amount of *N*-(*ar*-vinylbenzyl)-iminodiacetic acid, ammonium salt, was added. The samples were pigmented, applied to metal panels, baked, and exposed to the 95°F. water bath. There was no significant difference on any of these (Table VI).

Effect of pH of Latex

It was noticed that if the ammonium acrylate was not completely neutralized with NH_4OH , the resulting latex was inferior to others. Untreated styrene-butadiene latexes used in these experiments have a pH of 10-11.

TABLE VI
Effect of Dose Rate (5% Monomer Grafted)

Dose, Mrad	Dose rate (beam current), ma.	Adhesion	Rust resistance	Whitening resistance
2	0.1	Grade 1	Grade 1	Grade 1
2	1	" 1	" 1	" 1
2	5	" 1	" 1	" 1

TABLE VII
Effect of pH

Monomer	pH of grafted latex	Latex coagulated		
		Adhesion	Rust resistance	Whitening resistance
Ammonium acrylate	2			
	5	Grade 5	Grade 5	Grade 4
	8	" 3	" 3	" 3
	10	" 3	" 2	" 3
<i>N</i> -(<i>ar</i> -vinylbenzyl)-aspartic acid, NH ₄ salt	2			
	4	Grade 5	Grade 5	Grade 3
	6	" 4	" 5	" 3
	8	" 2	" 3	" 2
	10	" 1	" 1	" 1
<i>N</i> -(<i>ar</i> -vinylbenzyl)-iminodiacetic acid, NH ₄ salt	4	Grade 5	Grade 5	Grade 3
	6	" 4	" 5	" 3
	8	" 2	" 3	" 2
		" 1	" 1	" 1
	10	" 1	" 1	" 1

The grafted latexes were prepared as before, and the pH was adjusted with dilute NH₄OH, dilute acrylic acid (in ammonium acrylate grafts), and dilute acetic acid (in chelate grafts).

In general, in the pH range of 2-4, the latex was coagulated. At pH 4-6, the latex became very thick when the pigment dispersion was added. When these were applied to metal panels, the corrosion was accelerated. Satisfactory results were obtained with latexes in the pH range of 7-9, but those having a pH higher than 9 were superior. The results are shown in Table VII.

Effect of Styrene-Butadiene Ratio

A series of experiments was run to determine the effect of styrene to butadiene ratios in the latex. *N*-(*ar*-vinylbenzyl)iminodiacetic acid, ammonium salt, was grafted (5%) to the latexes by preirradiation techniques as previously described. The grafted latexes were pigmented, then applied to metal panels and baked at 300°F. for 30 min. These were evaluated

TABLE VIII
Effect of Styrene-Butadiene Ratios on Adhesion

	Styrene, %	Adhesion	
		Untreated	Grafted
A	25	Grade 2	Grade 1
B	55	" 3	" 1
C	60	" 3	" 1
D	66	" 3	" 1
E	80	" 5	" 4

TABLE IX
Effect of Styrene-Butadiene Ratios on Rust Resistance

	Styrene, %	Rust resistance	
		Untreated	Grafted
A	25	Grade 4	Grade 1
B	55	" 5	" 1
C	60	" 4	" 1
D	66	" 4	" 1
E	80	" 5	" 2

TABLE X
Effect of Styrene-Butadiene Ratios on Whitening Resistance

	Styrene, %	Whitening resistance	
		Untreated	Grafted
A	25	Grade 2	Grade 1
B	55	" 5	" 1
C	60	" 5	" 1
D	66	" 5	" 1
E	80	" 4	" 1

after 300 hr. in a 95°F. water bath. The results are shown in Tables VIII-X.

Another latex, containing 96% styrene was grafted with 5% *N*-(*ar*-vinylbenzyl)iminodiacetic acid, ammonium salt. The untreated latex is not film-forming, even when pigmented. When the coating was baked on the metal panel, it cracked and curled up in approximately $\frac{1}{8}$ in. sections all over the panel. The grafted latex remained smooth with good adhesion after it was baked.

Effect of Various Monomers

With all of the chelating monomers, it was necessary to make the ammonium or sodium salt so they could be dissolved in water.

Definite improvement was obtained over the untreated latex with all of the monomers which were grafted, but the chelating monomers gave better

protection than ammonium acrylate or ammonium methacrylate. The major difference in the latexes grafted with chelating monomers and those grafted with acrylates is in the fading of the pigmented coating (Table XI). The acrylate-grafted latexes show some whitening after exposure to 95°F. water, but the chelate-grafted latexes do not. The conclusion drawn is that the chelating compound gives better pigment binding than the acrylic salts. This is because the calcium oxide, aluminum oxide, and iron oxide in the pigment apparently do not react readily with the acrylate-grafted latex. All of these oxides are capable of forming complexes with the grafted chelating monomers, however. When the latex is applied to the metal, iron oxide begins to form. The acrylate salt is more stable than the oxide and forms preferentially, improving the adhesion. Since the chelate is even more stable than the acrylate salt, a better coating is formed. Thus, the surface of the metal is sealed, protected from oxidation, and a good bonding from the coating to the metal is obtained. The coatings prepared with untreated latex can usually be scraped from the panel with a knife, leaving a clean metal surface. In almost every case with a grafted latex, it was impossible to scrape the metal clean. Either some of the coating remained, or some of the metal was scraped off with the coating.

TABLE XI
5% Monomer Grafted to Styrene-Butadiene Latex

Monomer	Adhesion	Rust resistance	Whitening resistance
NH ₄ salt of <i>N</i> (vinylbenzyl iminodiacetic acid	Grade 1	Grade 1	Grade 1
NH ₄ salt of <i>N</i> (vinylbenzyl)-aspartic acid	" 1	" 1	" 1
NH ₄ salt of <i>N,N</i> -bis(vinylbenzyl)glycine	" 1	" 1	" 1
NH ₄ salt of 2-(vinylphenyl)-glycine	" 1	" 1	" 1
Ammonium methacrylate	" 1	" 2	" 3
Ammonium acrylate	" 1	" 2	" 3
None	" 4	" 5	" 5

Effect of Monomer Concentration

To study the effect of monomer concentration in the latex, we evaluated latexes containing 0.002–20 wt.-% ammonium acrylate (based on solids). *N*-(*ar*-vinylbenzyl)iminodiacetic acid and *N,N'*-bis(vinylbenzyl)glycine were evaluated on concentrations from 0.5–20%. It was determined from the results obtained in these experiments that all of the monomers give improvement from 0.5% to 10%, with a preferred range of 2–8% ammonium acrylate or ammonium methacrylate (4% was observed as the optimum). In the case of the chelating monomers, the preferred range is 4–8% and the optimum is 5–6%. The results are shown in Table XII.

TABLE XII
Effect of Monomer Concentration

Monomer	Concentration, wt.-%	Adhesion	Rust resistance	Whitening resistance
None	—	Grade 5	Grade 5	Grade 5
Ammonium acrylate	0.002	" 5	" 5	" 5
Ammonium acrylate	0.02	" 4	" 4	" 4
Ammonium acrylate	0.2	" 3	" 3	" 4
Ammonium acrylate	2.0	" 2	" 2	" 3
Ammonium acrylate	4-10	" 1	" 2	" 3
Ammonium acrylate	12	" 3	" 4	" 2
Ammonium acrylate	>12		Latex coagulated	
<i>N</i> -(<i>ar</i> -vinylbenzyl)-iminodiacetic acid, NH ₄ salt	0.5-2.0	Grade 2	Grade 2	Grade 2
	4-10	" 1	" 1	" 1
	>10	" 2	" 1	" 1
<i>N,N</i> -bis(vinylbenzyl)-glycine, NH ₄ salt	0.5-2.0	" 2	" 2	" 1
	4-8	" 1	" 1	" 1
	10	" 3	" 3	" 3
	>10	" 3	" 4	" 3

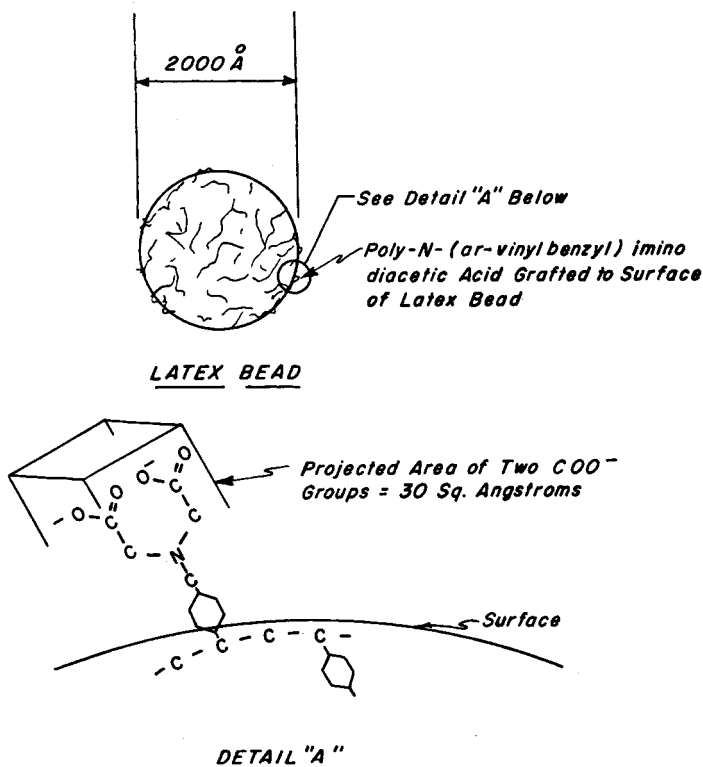


Fig. 4. Detail of surface,

It was theorized that in order to get maximum improvement, each latex particle should have at least a monomolecular layer of monomer grafted on the surface (Fig. 4). In order to calculate the amount of monomer necessary to form a monolayer of influence, we assumed: (a) the hydrophobic grafted chain is absorbed on the surface of the latex particle, and (b) the hydrophilic ionized chelate or acrylate groups are left free to extend from the particle and exert a definite area of influence. The area of influence was determined by using Godfrey molecular models which are scale models based on bond distances and Van der Waals radii. The ionized acrylate area of influence was calculated as 12 \AA^2 . For the ionized *N*-(*ar*-vinylbenzyl)iminodiacetic acid, the area was calculated as 30 \AA^2 . The average particle size of the latex is 2000 \AA . in diameter. Using these figures, the quantities necessary for a monolayer were 3.8% ammonium acrylate and 4.8% ammonium salt of *N*-(*ar*-vinylbenzyl)iminodiacetic acid. The method of calculating these is as follows.

$$\text{Average diameter of latex particle} = 2000 \text{ \AA}.$$

$$\text{Area of latex particle} = 1.26 \times 10^7 \text{ \AA}^2$$

$$\text{Volume of latex particle} = 4.18 \times 10^9 \text{ \AA}^3$$

$$\text{Weight of latex particle} = 4.18 \times 10^{-15} \text{ g. (assuming density} = 1 \text{ g./cc.)}$$

Then:

$$\text{Area of two } \text{COO}^- \text{ groups of } N\text{-(vinylbenzyl)iminodiacetic acid} = 30 \text{ \AA}^2$$

$$\text{Molecular weight of } N\text{-(vinylbenzyl)iminodiacetic acid} = 250$$

$$\text{Weight of } N\text{-(vinylbenzyl)iminodiacetic acid} = 4.16 \times 10^{-22} \text{ g./molecule}$$

$$\frac{1.26 \times 10^7 \times 4.16 \times 10^{-22}}{30 \times 4.18 \times 10^{-15}}$$

$$= 4.2 \times 10^{-2} = 4.2\% \text{ } N\text{-(vinylbenzyl)iminoacetic acid}$$

$$= 4.8\% (\text{NH}_4)_2 \text{ salt of } N\text{-(vinylbenzyl)iminodiacetic acid}$$

Also:

$$\text{Area of } \text{COO}^- \text{ group on acrylic acid} = 12 \text{ \AA}^2$$

$$\text{Molecular weight of acrylic acid} = 72$$

$$\text{Weight of acrylic acid} = 1.2 \times 10^{-22} \text{ g./molecule}$$

$$\frac{1.2 \times 10^{-22} \times 1.26 \times 10^7}{4.18 \times 10^{-15} \times 12} = 3.02 \times 10^{-2} = 3.02\% \text{ acrylic acid}$$

$$= 3.8\% \text{ NH}_4 \text{ acrylate}$$

Our thanks to R. A. Mock and L. R. Morris, C. C. Kennedy Research Lab., The Dow Chemical Company, Midland, for supplying the chelating monomers, and to Dr. A. E. Martell, Clark University, for helpful suggestions.

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Résumé

On a décrit antérieurement le greffage d'esters vinyliques à du caoutchouc naturel. Nous avons greffé deux autres types de monomères vinyliques à un caoutchouc styrène-butadiène. Ces monomères sont les sels d'ammonium des acides acrylique et méthacrylique et les sels d'ammonium d'agents de chélation vinylique tels que l'acide *N*-(*ar*-vinylbenzyl)imino diacétique (Des doses de radiation de 0.5 à 2 mégards ont été suffisantes pour effectuer le greffage). Ces monomères, dans une proportion de 2 à 6%, améliorent nettement leur adhésion aux métaux. Ils améliorent aussi leur résistance à la rouille, et lorsqu'ils sont pigmentés par une dispersion d'oxyde de fer, ils améliorent la résistance au blanchissement du revêtement. Les monomères de chélation vinyliques donnent le meilleur résultat sur du caoutchouc non traité, particulièrement en ce qui concerne la résistance au blanchiment. La quantité optimum de monomère varie de 4 à 6%. Ceci vérifie très bien la quantité théorique pour une couche monomoléculaire de monomère entourant chaque particule de caoutchouc.

Zusammenfassung

Über die Aufpfropfung von Vinylestern auf Naturkautschuk latex wurde schon früher berichtet. Nun haben wir zwei andere Arten von Vinylmonomeren auf Styrolbutadien-latex aufgepfropft. Diese Monomeren sind die Ammoniumsalze von Acryl- und Methacrylsäure und die Ammoniumsalze von Vinylchelatlignern, wie *N*-(*ar*-Vinylbenzyl)-iminodiessigsäure. (Ionisierende Strahlungsdosen von 0,5 bis 2 Mrad genügen zur Durchführung des Aufpfropfens.) Diese Monomeren ergeben im Bereich von 2 bis 6% eine sehr ausgeprägte Adhäsion an Metalle. Sie verbessern auch die Rostbeständigkeit, und bei Pigmentierung mit Eisenoxyddispersion wird die Beständigkeit gegen Weisswerden verbessert. Die chelatbildenden Polymeren ergeben die grösste Verbesserung gegenüber dem nicht behandelten Latex, speziell in bezug auf die Beständigkeit gegenüber Weisswerden des Überzugs. Die optimale Monomermenge liegt zwischen 4 und 6%. Das entspricht sehr gut der theoretischen, zur Bildung einer monomolekulare Monomerschicht um jedes Latexteilchen erforderlichen Menge.

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