Decomposable Crosslinking Paint: Waste Minimization

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A paint film crosslinked by a reaction between a carbonyl group and a hydrazide group could be easily decomposed by dipping it in a solution containing water, solvents, and acids. The method was studied to minimize the waste produced by the elimination of the decomposable paint film. This was performed in two steps: a dipping in aqueous solution containing solvents and acids, and a successive wash with solvents. Decomposition of the crosslinking bonds and the elution of the decomposed free crosslinker took place in the first dipping process, and the elimination of the decomposed resins in the second washing process. The aqueous solution could be used for a long time without contamination by the decomposed resins, and the decomposed resin could easily be recovered from the resin solution containing no other contaminants.

INTRODUCTION

Adhesion of paint films can interfere with the recycling of industrial materials. The use of decomposable crosslinking paints reported in previous papers[1,2] could eliminate this barrier and reduce industrial wastes. However, elimination of the decomposable crosslinking paint films may produce another kind of waste, that is, a solution containing decomposed resins, crosslinkers, etc. In this study, we tried to minimize the waste of not only industrial materials but also the decomposed components.

The new film elimination process was performed according to the procedure shown in *Figure* 1. First, a coated material was dipped in a crosslink-decomposing solution (CDS) composed of a solvent (swelling agent for the paint film), an acid (catalyst for crosslink scission), and water (reactant). The three components of CDS are the same as that of a film-decomposing solution (FDS) used in previous papers,[1,2] but the ratio of the three components was different. The components of both solutions penetrated the paint films and severed the crosslinking bonds. FDS rich in solvent could dissolve all the decomposed paint components such as uncrosslinked resin, crosslinkers, etc., while the CDS used in this study dissolved only hydrophilic crosslinkers, because the main CDS component was water, which did not dissolve hydrophobic resins. Only crosslinkers could be extracted from the decomposed paint film into CDS. As a result, uncrosslinked and swelling resins were left on the surface of the substrate materials which were picked up from CDS. It could easily be washed out with solvents in a subsequent process.

The useful life of the CDS could be prolonged much more than that of FDS, because the decomposed resin, which should be the main contaminant, was not soluble in CDS. On the other hand, recovery of the resin from the solution produced by solvent washing was very easy, since it did not contain other contaminants such as crosslinkers and acids.

The advantages of the new film removal processes, in comparison with the previous system by FDS, are as follows: (1) less flammability of CDS caused by high water content; (2) long life of CDS caused by immiscibility with the resins; and (3) easy recovery of the resins.

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EXPERIMENTAL

Materials

All of the materials used were of commercial grade and were not purified further. The abbreviations of materials used in the film removal processes are defined in *Table* 1. Poly(acrylonitrile-butadiene-styrene) (ABS) and Poly(methyl methacrylate) (PMMA) were supplied by Paltec Co., Ltd., and polypropylene panel (PP) by Mitsubishi Yuka Co., Ltd.

Preparation

Preparation of Resins: Ordinary laboratory equipment and preparation methods were used for the synthesis of the resins. Diacetone acrylamide (DAAm) was

Table 1—Definitions of Abbreviations

Crosslink-Decomposing Solutions

DIW ..... Deionized water
PTS ..... p-Toluenesulfonic acid monohydrate
PGPE ..... Propylene glycol monopropyl ether
PGME ..... Propylene glycol monomethyl ether
MEK ..... Methyl ethyl ketone
CHN ..... Cyclohexanone

Plastic Panels

PP ..... Polypropylene panel
ABS ..... Poly(acrylonitrile-butadiene-styrene) panel
PMMA ..... Poly(methyl methacrylate) panel

used as the monomer containing a carbonyl group. The copolymerizations were performed by the dropwise addition of a mixture of monomers and an initiator (azobisiso-butyronitrile) to propylene glycol monomethyl ether (PGME) at 110°C. The copolymers were neutralized with triethylamine, diluted by the addition of isopropanol, and then dispersed mechanically in water. The emulsions obtained were distilled under reduced pressure to eliminate the isopropanol. The properties and compositions of the copolymers used in this study are summarized in *Table* 2.

Preparation of Crosslinked Coating Films: Two-component clear paints of CC-261 were prepared by mixing the emulsions with 13% aqueous carbohydrazide (CH) solution or 16% aqueous adipic acid dihydrazide solution. The mole ratio of the hydrazide group in the crosslinker to the carbonyl group in the emulsion was 0.5. The paint was applied to polypropylene panel (PP) surfaces with a bar coater. The film thickness evaluated by the weights of the paint films was 25 μm for bar coater No. 18, 35 μm for No. 32, and 45 μm for No. 48.

Two-component white paints of CC-258 and CC-261 were prepared by mixing with 13% aqueous carbohydrazide solution and 68% aqueous titanium white paste. The mole ratio of the hydrazide and carbonyl groups was the same as that of the clear paint, and the additional amount of titanium dioxide was 50% of the resin weight. The film thickness of the white paint of CC-261 coated with bar coater No. 48 was 35 μm. The thickness of the white paint of CC-258 coated with bar coater No. 60 was 35 μm.

The coated panels were dried at 160°C for 30 min. After dipping in CDS, the panels were also dried under the same condition.

Preparation of Crosslink-Decomposing Solutions (CDS): CDS had to contain three components, that is, good solvents for the resins, water, and acids, in analogy with the FDS used in previous papers.[1,2] The difference between the two solutions was the water content. For the preparation of CDS, water was added until the decomposed paint resin became insoluble.

Measurements

Methods of Evaluating Film Change During Dipping Process: Objects covered by the crosslinking paint film were dipped in a CDS for a certain time at various temperatures. Residual weights of the decomposed paint films were measured after the following treatments: (1) drying for 30 min at 160°C, (2) washing with acetone after drying for 30 min at 160°C, and (3) washing with acetone without drying. The drying conditions were sufficient to eliminate the solvents and the water swelling in the decomposed paint film. It was confirmed that the PP used as a substrate was unharmed by these treatments; therefore, the reductions in weight of the test panels were attributed to the removal of paint film components. Some fractions of the gel resin were detached from the panel surface during the washing. Although they were also added to the residual weight, numerical values under 50% were uncertain because of the difficulty of complete collection. However, the confirmation of a zero point was rather easy.

When the test panels were dipped in the CDS, its components, i.e., solvent, water, and acid, penetrated into the paint film and decomposed the crosslinks. Hydrophilic decomposed products such as a free crosslinker were eluted from the decomposed paint film with CDS rich in water. Weight loss occurring due to Treatment 1 theoretically corresponded to the weight of the eluted crosslinker. Weight loss obtained by Treatment 3 corresponded to the removable weight of the thermoplastic

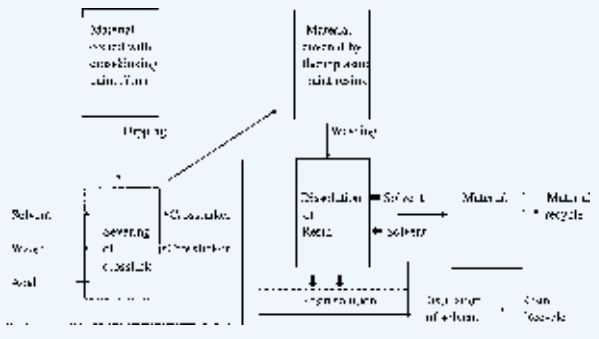

Figure 1—Elimination process of crosslinking paint film.

Table 2—Compositions and Properties of Diacetone Acrylamide Copolymers

Resin No.	CC-258	CC-261
DAAm (%)	30.0	31.1
AAc (%)	2.2	2.2
St (%)	0	23.8
n-BA (%)	24.4	42.9
MMA (%)	17.4	0
EA (%)	26.0	0
T_g (°C)	10	10
Acid value	17	17
Mn	9400	12000
pH	8.9	9.5
Solid content (%)	36.8	47.6

Note: %: by weight T_g, Arithmetic mean of homopolymer T_gs of component monomers, Mn: values estimated on the basis of GPC data.
Key: DAAm: Diacetone acrylamide; AAc: Acrylic acid; St: Styrene; n-BA: n-Butyl acrylate; MMA: Methyl methacrylate; EA: ethyl acrylate.

paint resins and pigments, which were produced by the decomposition of the paint film. Uncrosslinked paint resin could be easily washed out with acetone because of the low molecular weight of the original paint resins.

A measurement of Treatment 2 was carried out in order to confirm the elimination of the free crosslinker from the decomposed paint resin phase. Even if only a slight amount of the crosslinker was left in the decomposed resin phase, recrosslinking reactions should occur on heating to dry the test panel.

Elution % of Plastic Panel: The elution % of the plastic panel was the weight loss caused by the dissolution of the plastic material. The weight loss was estimated by the following equation:

$$\text{Elution \%} = (B–A) / A \times 100$$

where A is the weight of the original plastic panel and B is the weight of the same panel measured after dipping in CDS under certain conditions and drying for one hour at 200°C. It was confirmed that the drying conditions were sufficient for the evaporation of the swelling solvents and caused no serious damage to the plastic polymers. The weight losses determined by the blank test (drying for one hour at 200°C) were as follows: PP = 0.2%, PMMA = 0.8%, and ABS = 0.5%. The correction values were substrated from the experimental data.

Swelling % of Plastic Panel: Plastic panels were swollen by the solvents during film elimination. The extent of the swelling was evaluated by the following equation, if the elution of the plastic panels was not large:

$$\text{Swelling \%} = (C–A) / A \times 100$$

where C is the weight of the swelling panel. To get an accurate swelling value, the excess surface solvent was evaporated for 20 min at 60°C. The weight of the swollen panel remained unaltered during the drying at 60°C.

Properties of Coating Films: A pencil hardness test was performed according to the Hand Scratch Method[3] of JIS K5400. The Erichsen value[4] was the pushing distance without cracking. The procedure was done according to JIS K5400. Impact strength was measured by DuPont Method[5] of JIS K5400. For adhesion, the Cross Cut Test[6] of JIS K5400 was used. Solvent resistance was estimated based on the appearance of the test film after the evaporation of two drops (about 0.05 ml) of the acetone placed on the paint films. Water resistance was estimated by the surface appearance of the dry film after immersing in DIW for a fixed time.

RESULTS AND DISCUSSION

Properties of Coating Films

The crosslinking reaction between the carbonyl and hydrazide groups was actually used for reinforcing one-component emulsion paints.[7,8] A two-component paint was also reported.[9,10] The properties of typical coating films used in this work are summarized in *Table* 3. Although the properties vary depending on the composition of the resin, molecular weight, crosslinking density, etc., the results indicate that the decomposable paints meet the basic requirements of a paint for normal use.

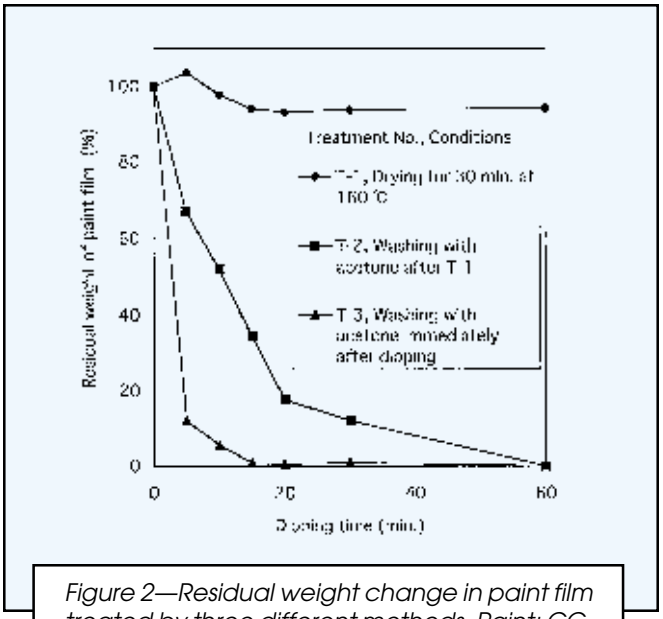

Figure 2—Residual weight change in paint film treated by three different methods. Paint: CC-261 clear; film thickness: 45 μm; CDS composition: DIW/PGPE/PTS = 75/20/5; dipping temp: 80°C.

Elimination of Coating Films

Fundamental Meanings of Three Treatments: *Figure* 2 shows the weight changes in the paint film remaining on the substrate after each treatment, symbolized by T-1, T-2, and T-3.

Fifteen minutes are needed to attain a zero value of T-3 which indicates the completion of paint film decomposition. On the other hand, the weight loss estimated by T-1, corresponding to the weight eluted from the paint film by CDS, remained constant at about six percent after 15 min. This value is slightly larger than four percent corresponding to the maximum weight of the crosslinker in the paint film. The difference of two percent may be based on the dissolution of the hydrophilic part of the resin. The early attainment of a constant value indicates that most of the free crosslinkers pro-

Table 3—Properties of Coating Films

	White Paint of CC-261	White Paint of CC-258
Film thickness	35 μm	35 μm
Pencil hardness	H	2H
Erichsen values	7 mm<	7 mm<
Impact strength (1 kg, 1/2 ϕ)	10 cm	20 cm
Adhesion	100/100	100/100
Solvent resistance	No change	No change
Water resistance (6 h)	No change	Blister trace
Initial gloss (60°)	80	85

Substrate: Zinc-phosphated cold-rolled steel (thickness = 0.8 mm).

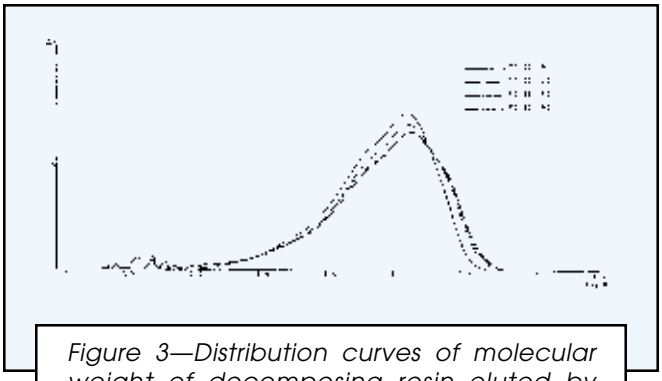

Figure 3—Distribution curves of molecular weight of decomposing resin eluted by acetone. Paint: CC-261 clear; CDS composition: DIW/PGPE/PTS = 75/20/5; dipping temp: 80°C; dipping time: last letters of labels indicate dipping time (min).

duced by the paint film decomposition are eluted from the paint film by CDS as soon as they are generated. When the dipping time exceeds 15 min, most of the original paint components remain on the surface of the substrate and can be easily eliminated by washing with a solvent. Thus, the decomposed free crosslinker is the only major contaminant of CDS. In any event, one intention of this report, i.e., extension of CDS lifetime, can be achieved by this two-step elimination method.

On the other hand, 60 min is necessary to attain zero percent of T-2, where thorough elution of the free crosslinker is required to inhibit the recombination promoted by the heating for the film drying. Another intention of this report is the easy recycling use of the resin due to the complete separation of the crosslinker, which requires a 60 min dipping in CDS at 80°C.

The molecular weights of the decomposed resins recovered from the acetone solution obtained with T-3 were measured. *Figure* 3 shows the results in comparison with the original resin molecular weight. The original resin was also recovered from the acetone solution, which was obtained by dissolution of the dry film without a crosslinker. In this case, the decomposed resins could not be linked again by the free crosslinker remaining in the paint residue during the evaporating process of acetone to isolate the resin, because the hydrazide groups of the crosslinkers were blocked by the carbonyl groups of acetone. The molecular weights of the decomposed resins became nearly the same as that of the original resin. The values were already attained by 30 min dipping. This result indicated that the decomposition of the crosslinking bonds had finished within 30 min. On the other hand, when the isolation of the resin after 30 min dipping was performed using toluene, which does not have blocking ability for the hydrazide group, the isolated resin was not dissolved in any solvents. This phenomenon indicated that the resins decomposed by 30 min dipping were recombined with the free crosslinkers remaining in the paint residue. The decomposed resins recovered with toluene after 90 min dipping had nearly the same molecular weight as the original one as shown in *Figure* 4. This means the complete absence of free crosslinkers in the paint residue. The slight difference between the two molecular weights of the resins recovered from acetone and toluene solutions results from free crosslinkers which were dissolved in water droplets adhering to the substrate surface. The hydrophilic crosslinkers were incorporated with the water in acetone solution. Toluene was separated from the water phase.

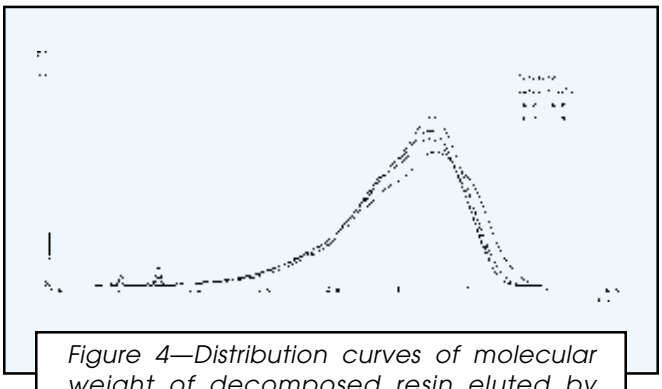

Figure 4—Distribution curves of molecular weight of decomposed resin eluted by acetone and toluene. Paint: CC-261 clear; CDS composition: DIW/PGPE/PTS = 75/20/5; dipping temp: 80°C, CC-261-0; original resin, CC-261-160°C: recovered resin from dry film heated for 30 min at 160°C without crosslinker, CC-261-K-90: decomposed resin recovered with acetone after 90 min dipping in CDS shown in Figure 3, CC-261-T-90: Decomposed resin recovered with toluene after 90 min dipping in same CDS.

The film-decomposing processes referred to in *Figures* 3 and 4 were consistent with the results of *Figure* 2. The determination of free CH dissolving in CDS was also attempted by high performance liquid chromatography (HPLC) using the absorption of 235 nm. However, it was not successful because of the overlapping of the absorption.

Influence of Paint Film Thickness: *Figure* 5 shows the influence of the paint film thickness on the residual weight changes. Although the effects of the thickness were not large, a lag was observed with increasing film thickness. As mentioned in the previous paper,[1] the effect of film thickness became clearer for slightly swollen film than for an extensively swollen one, where the reaction rate was the rate-determining step rather than the penetrating rate. The film swollen by CDS containing a small amount of solvent may not be sufficient for free passage of acid, water, and a decomposed free crosslinker. This could be presumed by observation of the paint film condition. The dipping film wrinkled slightly in the earlier stage and then stuck to the substrate with dipping time. *Figure* 5 may be considered as the result for the intermediately swollen samples.

Influence of Paint Components: *Figure* 6 shows the residual weight changes measured for two paints composed of different type resins. Resin CC-261 copolymerized with a large amount of styrene and n-butyl methacrylate should be more hydrophobic than Resin CC-258 containing a large amount of methyl methacrylate and ethyl acrylate.

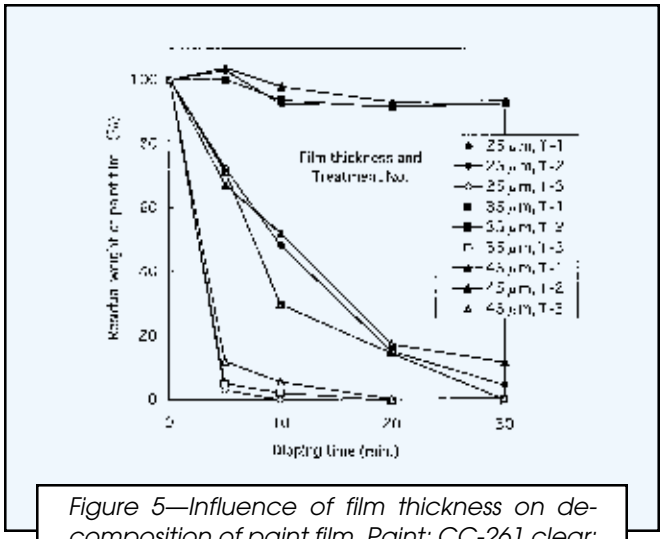

Figure 5—Influence of film thickness on decomposition of paint film. Paint: CC-261 clear; CDS composition: DIW/PGPE/PTS = 75/20/5; dipping temp: 80°C.

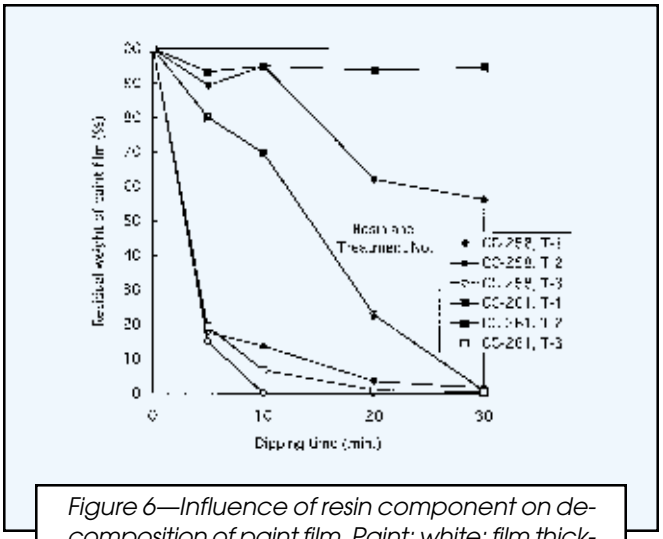

Figure 6—Influence of resin component on decomposition of paint film. Paint: white; film thickness: 35 μm; CDS composition: DIW/PGPE/PTS = 75/20/5; Dipping temp: 80°C.

When paint films were swollen too much by the solvent, some parts of them occasionally fell from the panel surface as droplets during handling. The large weight losses of CC-258 by T-1 were caused by this phenomenon. The paint film of Resin CC-258 absorbed substantial PGPE from CDS because of good compatibility between the resin and the solvent. This property also accelerated the weight losses by T-2 and T-3.

Influence of Crosslinker Properties: Two crosslinkers which had different solubility in water were used. One hundred grams of water can dissolve 32 g of carbohydrazide (DC) and 12 g of adipic acid dihydrazide (ADH) at 25°C. It is shown in *Figure* 7 that when the results of T-1 were compared, the paint film crosslinked by ADH loses about five percent more than that crosslinked by CD. This value corresponds roughly to the additional weight difference caused by the molecular weights of the crosslinkers, that is, 174 for ADH and 90 for CD.

The dipping times in which all paint film components disappeared by T-3 were 20 min for these two crosslinkers.

The values obtained by T-2, which were measured by the elution degree of the decomposed free crosslinker, were larger for ADH than for CH. These data were, therefore, in conflict with our expectation that the hydrophilic crosslinker should be easily eluted from the decomposed paint film into aqueous CDS. This may be explained by the lower crosslinking density than that corresponding to CH, because the insufficient solubility of ADH in water caused its isolation on the film surface without crosslinking reactions during the drying process.

Effect of Solvents in CDS: In *Figure* 8, three solvent species were used to test the effects of the film decomposition process by CDS. The weight loss rates by T-2 and T-3 of PGME were much slower than that of PGPE. The poor swelling property of PGME as shown in previous papers[1,2] was responsible for these results.

In the case of MEK, the film decomposing processes proceeded much faster than that with the other two solvents. This result could be explained by the strong swelling property of MEK. Quantitative measurements were difficult at 60 and 80°C because of the fragility of the extensively swollen film. The characteristics of the results measured at 40°C were the slow rate of T-2 and the fast rate of T-3, in comparison with the other two solvents. This indicates that, though the decomposing rates by MEK are fast, the elution of the decomposed free crosslinker is slow. MEK accelerates the rate of the T-2 with good swelling of the paint film. At the same time, the swollen paint phase changed its shape from a thin film to an oily mass during the dipping time. This transformation made it difficult to elute the decomposed free crosslinker.

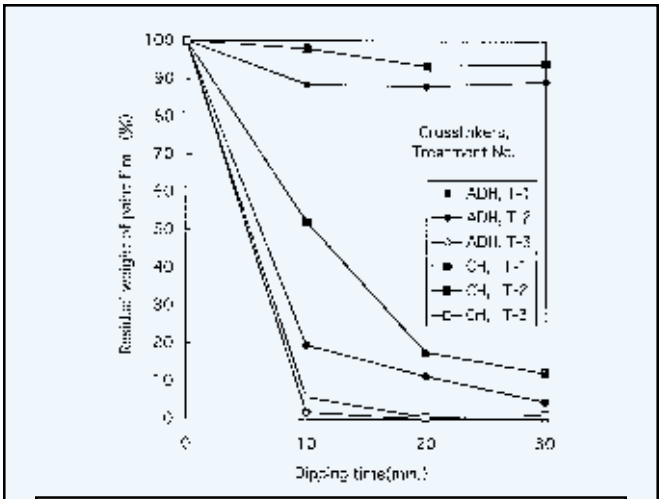

Figure 7—Influence of crosslinker species on decomposition of paint film. Paint: CC-261, clear; film thickness: 45 μm; CDS composition: DIW/PGPE/PTS = 75/20/5; dipping temp: 80°C; ADH: adipic acid dihydrazide, CH: carbohydrazide.

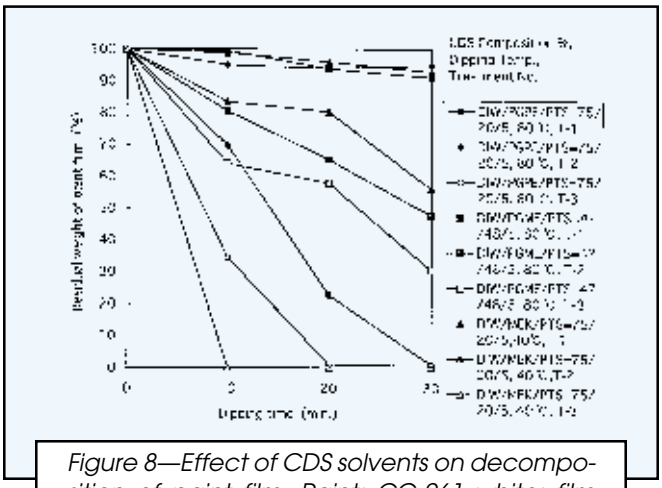

Figure 8—Effect of CDS solvents on decomposition of paint film. Paint: CC-261 white; film thickness: 35 μm.

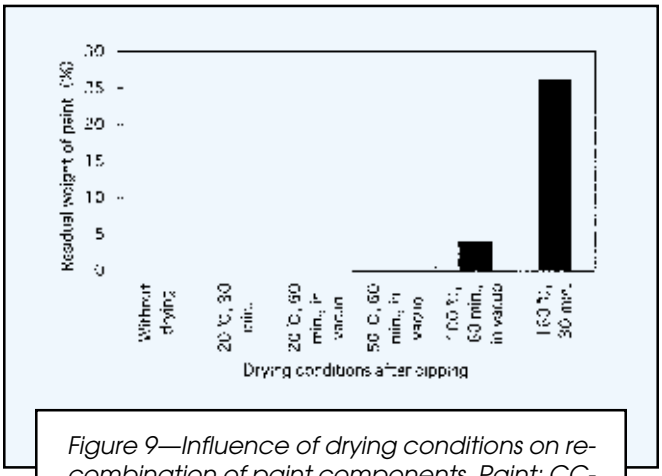

Figure 9—Influence of drying conditions on recombination of paint components. Paint: CC-261; film thickness: 45 μm; dipping conditions: in CDS: DIW/CHN/PGME/PTS = 65/10/20/5 for 10 min at 80°C.

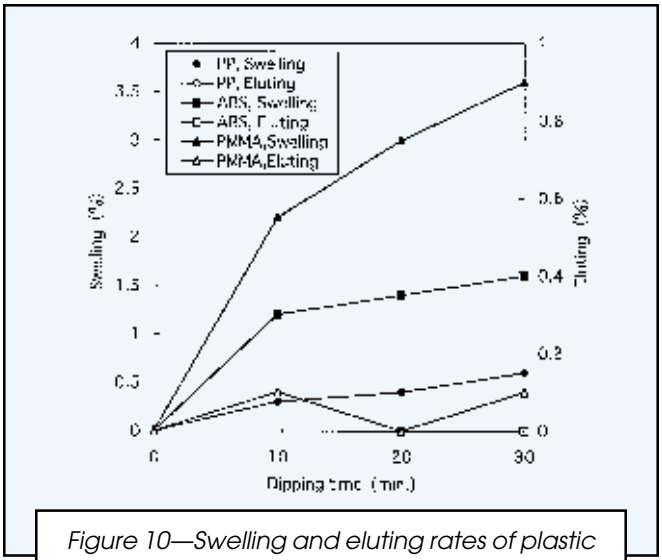

Figure 10—Swelling and eluting rates of plastic panels by dipping in CDS. CDS composition: DIW/PGPE/PTS = 75/20/5; dipping temp: 80°C; panel thickness: 2.5 mm.

MEK containing a carbonyl group can mask the dihydrazide crosslinker. However, the drying conditions of 30 min at 160°C are sufficient to reactivate it with heat degradation. *Figure* 9 shows the influence of drying conditions on the recombination of decomposed paint components. The sample panels were dipped in CDS containing CHN for 10 min at 80°C. The dipping conditions were adequate to obtain a zero value of T-3, but not sufficient for T-2. When the drying temperature exceeded 100°C, the residual weights appeared, which should result from a recombination of the resin with the deblocked crosslinker.

Damage to Plastic Panel During Dipping in CDS

When thermoplastic panels were used as a coating substrate, they were damaged by the solvents in CDS during the dipping time. The damage was evaluated by two measurable values, that is, weight increases due to the swelling with CDS solvents and weight loss due to the plastic polymer elution into CDS. The extent of damage to the coating substrate can be estimated by dipping the uncoated substrate[11] in the same CDS.

Figure 10 shows the swelling and eluting rates of three thermoplastic panels dipped in CDS which were used in *Figure* 4. The results of *Figure* 4 indicate that dipping 10 min at 80°C was sufficient to decompose all crosslinking bonds. The swelling and eluting of each plastic panel for 10 min dipping were estimated from *Figure* 10 as follows: the swelling degrees of PP, ABS, and PMMA are 0.3, 1.3, and 2.2%, respectively. Elution was low for all these plastic panels.

CONCLUSIONS

In the paint film-decomposing method by dipping in CDS, the dihydrazide crosslinkers and the paint resins could be separately eluted in CDS and in the washing solvents, respectively. As a result, the amount of contamination in CDS was small and its useful life should be substantially extended. When the elution of the crosslinkers was finished completely, the resin recovered by simple evaporation of the solvents may be directly reused because of the absence of the crosslinker.

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