

The Mechanical Properties of Films and Their Relation to Paint Chipping

HOWARD S. BENDER, *General Motors Research Laboratories,
Warren, Michigan*

Synopsis

A correlation has been made between dynamic mechanical properties and impact resistance of a multicoat paint system. It has been determined that the shear or rigidity modulus and damping of free primer films are some of the parameters that control the impact characteristics of the system. Those films of low modulus and high damping show the best chip resistance. A series of physical and chemical modifications were made on the primer and chipping results were compared with dynamic mechanical properties of free paint films. It was found that increasing cure temperature, addition of catalysts, decreasing the oil length of the resin, increasing the amount of pigmentation and increasing the tension and strain rate all led to increased paint chipping and increases in the modulus of rigidity. Two new primers were synthesized which incorporated the above results and were found to give increased gravel impact resistance.

INTRODUCTION

It is well known that by changing certain parameters in surface coatings and the painting process, i.e., bake temperature, thickness, amount of catalysts added and pigment level, it is possible to change the chip resistance of the multicoat system. In reality, the mechanical properties of the paint film are being changed and these in turn are governed by the physics and chemistry of the system. This paper described investigations of the above mentioned parameters and their relation to paint chipping. In view of the results obtained, two experimental primers were prepared and subjected to impact testing.

The instrument used for impact testing of surface coatings is the S.A.E. J-400 Gravelometer, which has recently been adopted as an industry-wide testing machine.¹ The instrument is semiquantitative and serves the function of separating coatings as to their resistance to gravel impact. One pint of road gravel ($\frac{3}{8}$ -in. minimum— $\frac{5}{8}$ -in. maximum) was impacted against a test panel at 0°F, one foot away, by placing the gravel in an 80 psi air stream. Visual observations of some S.A.E. gravelometer panels indicated that the chip resistance of the paint system was intimately tied to the stiffness of the paint vehicle and its glass transition temperature (T_g). The latter term denotes the temperature range where a viscoelastic material changes from a glass of high modulus, low elongation and high tensile strength to a rubber of low modulus, high elongation and low tensile strength.

Impact resistance of polymeric materials has been predicted by a variety of low velocity and frequency procedures. Evans, Mara, and Bobalek² were able to correlate falling weight impact with low-speed tensile data on a variety of thermoplastic materials with reasonable accuracy. Bobalek and Evans³ examined seven engineering plastics as to their impact resistance by a variety of low-speed tests. Turley⁴ has studied the effect of polymer structure on impact properties by low-frequency dynamic mechanical testing. Special emphasis was placed on polymer transitions, temperature, and frequency variations.

An alternative procedure to determining the chip resistance of paint films would be by the use of high-speed testing as the Gravelometer test is run at high velocity (60–70 ft/sec).

In reviewing the methods available for determining the mechanical properties of viscoelastic materials, it was felt that the best way to achieve the desired results would be through the use of dynamic mechanical testing at low frequencies. Dynamic testing offers the possibility of observing transitions and, in particular, secondary transitions which are believed to be important in obtaining impact resistance in polymers.^{5,6}

A torsional pendulum was constructed and is described in the experimental section. One characteristic of the pendulum is that it is inverted or counterbalanced. In this way, free paint films can be tested. Only a limited amount of work with dynamic testing has occurred in the surface coatings industry. Zorll⁷ found that as alkyd melamine resins were increasingly pigmented the shear modulus and, hence, the T_g increased while damping also increased. Chen and Kumanotani⁸ examined the viscoelastic properties of fatty acid-modified alkyds and found that films prepared by the fatty acid method had a higher T_g than films prepared by the monoglyceride method. It was suggested that the molecular weight distribution of films prepared by the former method would be narrower, leading to more cross-linked structures and a higher T_g . In an earlier paper,⁹ the same authors found that as the oil length of alkyds increased, the glass transition temperature decreased, and as the molecular weight increased, so did the T_g . Hansen,¹⁰ has examined the effect of plasticizer on surface coatings supported on metal foil, while Pierce and Holsworth¹¹ examined the dynamic mechanical behavior of coatings intended for different applications.

It was felt that an excellent method of measuring the mechanical properties of films was by use of a counterbalanced torsional pendulum (Fig. 1). One end of the specimen is rigidly clamped while the other end is attached to an inertia disc which is free to oscillate. The time required for one complete oscillation is the period P . The shear modulus may be calculated from the period—the shorter the period, the greater the modulus. For rectangular samples,¹² the shear modulus G' can be calculated from the equation:

$$G' = \frac{IL(2\pi/P)^2}{W \times T^3[16/3 - 3.36(T/W) (1 - T^4/12W)]}$$

where:

- I = moment of inertia
- L = length of sample
- P = period of sample
- W = width of sample
- T = thickness of sample

In cases where the width is at least 100 times as large as the thickness, the equation reduces to:

$$G' = \frac{IL(2\pi)^2}{W \times T^3 \times 5.333 \times P^2}$$

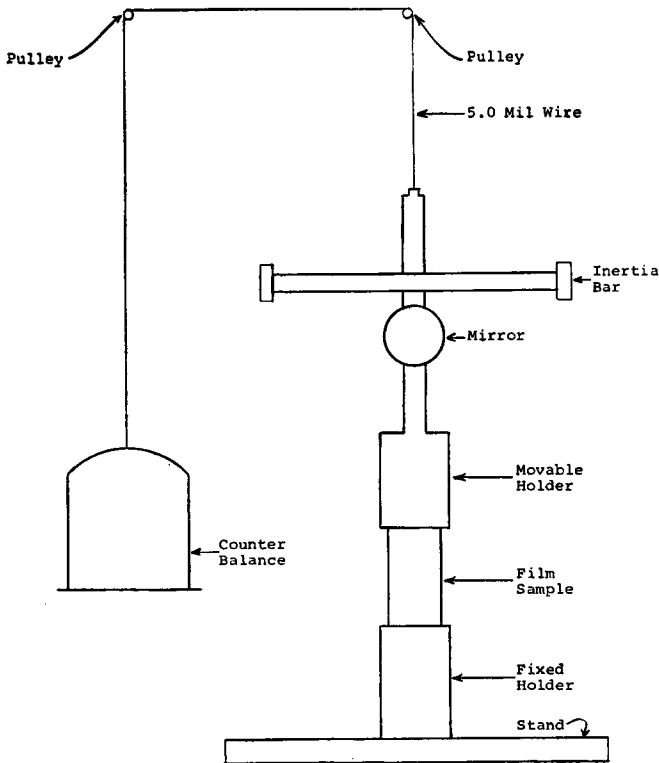


Fig. 1. Schematic diagram of a counterbalanced torsional pendulum.

Because of damping which gradually converts mechanical energy of the system into heat, the amplitude of the oscillations will decrease with time. Damping, expressed as logarithmic decrement Δ , is calculated from the natural log of the ratio of the amplitude of two successive oscillations.

$$\Delta = \ln A_1/A_2 = \ln A_2/A_3 = \ln A_n/A_{(n+1)}$$

Another damping term that is sometimes reported is the loss tangent (δ), defined as:

$$\delta = \Delta/\pi = G''/G'$$

where:

G'' is the loss modulus

As previously mentioned, it is our feeling that paint chipping by stone impact is intimately connected with the glass transition temperature of the paint vehicle. Below T_g , thermal energy is not available to allow segments of the chain to move as a whole. The motion of individual atoms is limited to small excursions around their equilibrium position. The polymer exhibits high modulus and low damping. The induced stress cannot be relaxed and the film shatters. As the temperature approaches T_g , increased thermal energy becomes sufficient to allow larger molecular motions. The modulus decreases sharply with temperature, while damping increases. Induced stresses can be relieved somewhat more easily and the amount of paint chipping is dramatically reduced.

EXPERIMENTAL

Resin Preparation

50% Oil Length Soya Oil Alkyd. In a 1000-ml resin flask equipped with a heating mantle, condenser, Dean-Stark trap, stirrer, thermometer and nitrogen inlet was added 161.7 g (1.091 moles) of phthalic anhydride. After heating to 135°C, 235 g (0.840 moles) of soya oil fatty acid, 103.3 g (1.125 moles) of glycerol and 24.3 g (15% excess) of phthalic anhydride was added. This mixture was heated at a rate of 1°C/min until a temperature of 240°C was reached. The reaction was run at this temperature for 13 hr until an acid number of 6.1 and a viscosity of Z_1-Z_2 (50% solids in xylene) on the Gardner bubble viscometer was reached. During this time, 24.3 g (70.1%) of water was collected. To the resin was added 325 g of mineral spirits.

60% Oil Length Soya Oil Alkyd. The same equipment and procedure as previously described was employed. The amounts of monomers used were: 133.1 g (0.900 moles) of phthalic anhydride, 280 g (1.000 moles) of soya fatty acid and 86.9 g (0.944 moles) of glycerol. This mixture was heated at 240°C for 23.5 hr, until an acid number of 7.4 and viscosity of A was reached. During this time, 22.3 g (65.4%) of water was collected. After cooling, 325 g of mineral spirits was added.

70% Oil Length Soya Oil Alkyd. The same equipment and procedure as previously described were employed. The amounts of monomers were: 329.4 g (1.158 moles) of soya fatty acid, 98.8 g (0.667 moles) of phthalic anhydride and 76.8 g (0.836 moles) of glycerol. The reaction was heated at 240°C for 13 hr until an acid number of 7.6 and a viscosity of Z_1-Z_2

(100% solids) was obtained. During the reaction, 16.5 g (50.3%) of water was collected.

Impact-Resistant Alkyd Resin Containing Polyesters. The same equipment and procedure as previously described were employed in this experiment. The amounts of monomers used were: soya fatty acid 225 g (0.804 moles), phthalic anhydride 139.8 g (0.944 moles), glycerol 85.2 g (0.926 moles) and poly(ethylene adipate) (M.W. 4500) 50 g (0.011 moles). The dibasic acid and polyester were heated to 145°C and the fatty acid and glycerol slowly added. This mixture was heated to 205°C for 18 hr until an acid number of 9.9 and a viscosity (50% xylene) of Z_3 on the Gardner bubble viscometer was reached. During the reaction, 18.9 g (60.3%) of water of esterification was collected. After cooling, 325 g of mineral spirits was added to the resin.

Impact-Resistant Alkyd Resin Containing Polyethers. The procedure and equipment previously described was again employed. The amounts of monomers used were: 225 g (0.804 moles) of soya fatty acid, 140 g (0.945 moles) of phthalic anhydride, 85 g (0.925 moles) of glycerol and 50 g (0.0835 mole) of poly(oxyethylene) m.w. 600 were used in this experiment. The reaction was run at 240°C for 22 hr until an acid number of 7.5 and a viscosity (Gardner bubble viscometer) of 0 (50% xylene) were obtained. During the reaction, 17 g (53.9%) of water of esterification was obtained. After cooling, 325 g of mineral spirits was added to the resin.

Preparation of Paint from Impact-Resistant Resins

The two impact-resistant resins were converted to black alkyd primers by the addition and grinding of pigments. The pigment paste of the polyester alkyd resin was prepared from a mixture of 159.8 g of calcium carbonate and 20.2 g of carbon black. To this was added 82.5 g polyester alkyd (54.5% solids) and 37.5 g of mineral spirits. This gave a 60% pigment, 15% vehicle and 25% solvent mixture. This was shaken with 750 g of steel shot for 15 min, cooled and filtered to give 233 g of pigment paste with a Hegman particle size reading of 0.5 mil. To the paste was added 104.7 g of polyester alkyd resin to give a pigment-to-binder ratio of 100/100 (P/B). The pigment paste of the polyether alkyd resin was prepared in the same manner as described previously: 81.4 g (55.3% solids) of resin, 159.8 g of calcium carbonate, 20.2 g of carbon black and 37.5 g of mineral spirits were shaken for 15 min with 750 g of steel shot, cooled and filtered. Two hundred fifty-four grams of paste were collected which gave a Hegman reading of 1.0 mil. To the paste was added 114.1 g of polyether alkyd resin which gave a P/B of 100/100.

Preparation of Alkyd Primers with Varying Degrees of Pigmentation

A pigment paste of P/B 219/100, 63% solids and an alkyd resin 39.2% solids were obtained from a commercial supplier. By mixing the appropri-

TABLE I
P/B Ratio

<i>P/B</i> <i>B</i> = 100	Parts pigment paste	Parts clear resin	PVC ^a %	Calculated % solids	Observed % solids
0	0	100.0	0	—	32.8
25	100	392.0	10.51	43.9	44.0
50	100	170.8	17.35	47.9	49.2
75	100	97.3	23.95	51.2	51.3
100	100	59.6	29.55	53.3	54.3
150	100	21.3	38.70	58.8	58.9
200	100	5.0	45.65	61.8	61.4
219	100	0	47.30	—	63.0

^a Pigment volume concentration.

ate amounts of pigment paste and clear resin, a series of varying *P/B* ratios were prepared. This is shown in Table I.

Preparation of Alkyd Primer with Varying Degrees of Cross-Linking Catalysts

A sample of alkyd primer was obtained from a commercial supplier. Varying amounts of cross-linking catalysts were added. This is tabulated in Table II.

TABLE II
Catalysts Added

Sample number	Grams of solid soya fatty acid	% Co	g Co	% Pb	g Pb	% Mn	g Mn
1	64.5	0.05	0.536	0.10	0.268	0.025	0.268
2	62.5	0.10	1.044	0.20	0.522	0.05	0.522
3	67.4	0.20	2.242	0.40	1.121	0.10	1.121

Preparation of Chipping Panels

All primers were reduced with mineral spirits to a viscosity which would give a paint wedge, when dipped, of 0.4 to 0.7 mil. The primed panels were then baked at three temperatures; 350, 400 and 450°F for 30 min. After cooling, they were sealed with acrylic sealer, followed by acrylic white topcoat and baked at 275°F for 30 min. The thickness of the sealer and topcoat were carefully controlled: 0.3 mil of sealer and 2.4–2.6 mils of topcoat were applied.

Chipping of Panels

All panels were conditioned at 0°F for at least one hour prior to chipping. They were chipped in the SAE 400 Gravelometer.¹ The panels were rated by standard rating procedures.¹³

Preparation of Free Films

Primer films were cast on untreated, polished steel panels. The panels were first cleaned with high purity acetone and then sprayed with MS-122, W. R. Grace & Co., fluorocarbon release agent. The films were cast with a draw down blade, allowed to dry for 24 hr, and baked at 350, 400 and 450°F for 30 min in a horizontal position. After cooling, the films were removed by placing a razor blade under the film and gently prying the film free from the substrate. The film thickness was measured with a micrometer to the nearest 0.1 mil. Those areas which were 2.0 mils \pm 0.1 mil were cut into 0.5-in. strips of one- to two-inch lengths, and conditioned at 72°F and 50% relative humidity for at least 72 hr.

Testing of Films

The films were tested on a counterbalanced torsional pendulum (Fig. 1). The pendulum consisted of a fixed sample holder, a moveable holder, torsion arms, mirror, tungsten wire, two pulleys, and a counterbalance. Readout was obtained by a parallel monitoring concept. An uv light was fixed onto the mirror and rebounded onto ultraviolet light sensitive paper. In this way, the decay curves of the sample could be followed. The moment of inertia of the pendulum was determined using a quartz rod of known length, diameter, and shear modulus. For this instrument, the moment of inertia was found to be 723.25 g cm.²

TABULATION OF RESULTS

By measuring the length, width, thickness, period, and amplitude of the sample and the moment of inertia of the pendulum, it was possible to calculate the shear modulus (G'), damping (Δ), and loss tangent (δ) of the sample.

RESULTS AND CONCLUSIONS

Our results indicate that by changing the chemistry and physics of the paint system it is possible to change the impact characteristics of the surface coatings. The results reported here are some of the experiments that were performed on primers. In all cases, when sealer and topcoat were used, the same materials and thicknesses were employed. The thickness of these materials are crucial to obtaining reproducible chip resistance.

Table III indicates the different physical and chemical modifications of primers that were made and correlates the dynamic mechanical properties with gravelometer results. As tension is applied to the free film, the shear modulus (G') increases while the damping decreases. This is illustrated in Figure 2. This can be considered similar to increasing the velocity of impact, which obviously increases chipping.

By increasing the curing temperature, decreasing the thickness of the primer film, or adding catalysts, such as naphthonic acid salts, cross-linking of the primer occurs. This leads to increases in the shear modulus, whereas

TABLE III
Dynamic Mechanical Properties and Impact Results

Test	Sample ^a	G' × 10 ⁹ dynes/ cm ²	Δ	× 10 ⁻²	Chip- ping ^b
Tension on sample, g	20	2.09	0.442	14.05	—
	30	2.58	0.289	9.20	—
	40	3.35	0.189	6.02	—
	50	4.13	0.155	4.94	—
	70	5.97	0.101	3.22	—
	100	8.77	0.072	2.29	—
Primer thickness, in.	0.0021	3.41	0.201	6.40	—
	0.0024	2.58	0.289	9.20	—
	0.0027	1.81	0.324	10.31	—
Cure temperature, °F	30@350	3.41	0.201	6.40	6
	30@400	3.68	0.154	4.93	5
Catalyst	Present ^c	3.90	0.046	1.49	3
	Absent	3.41	0.201	6.40	5
Pigment volume concentration, %	10.51	3.45	0.063	2.00	7
	17.35	4.13	0.075	2.38	6
	23.95	4.90	0.087	2.77	6
	29.55	4.40	0.090	2.87	5
	38.70	4.60	0.140	4.45	6
	45.60	4.72	0.115	3.65	5
Oil length, %	47.30	5.08	0.207	6.59	4
	50	3.38	0.065	2.05	4
	60	3.20	0.084	2.76	6
	70	2.77	0.134	4.27	7

^a All films were 0.002 ± 0.0001 in. unless otherwise stated.

^b An increase in ratings denotes an increase in chip resistance.

^c 0.1% cobalt naphthonate; 0.2% lead naphthonate; 0.05% manganese naphthonate.

damping decreases. The primer becomes brittle and is subject to glassy fracture. This can be seen in the impact results. It has also been shown that as increasing amounts of catalysts are added to cross-linking resins, the shear modulus becomes constant. This has been shown by gravelometer tests; by adding large amounts of catalyst, the impact results can be equalized regardless of the curing temperature.

Also investigated was the effect of varying the pigment volume concentration on the mechanical properties of paint films (Fig. 3). As the amount of pigment present was increased, the shear modulus increased. This concept of increasing stiffness with increased filler loading is well known in polymer chemistry^{14,15} and has recently been applied to paint chemistry.^{7,16} Interestingly, the damping increases with increasing pigment loading. It is believed that this is due to the pigment particles slipping over one another causing friction and heat. This theory has been applied in rubber chemistry to explain increases in the dissipation factor with higher concentrations of carbon black. This increase in damping can be used to explain why ap-

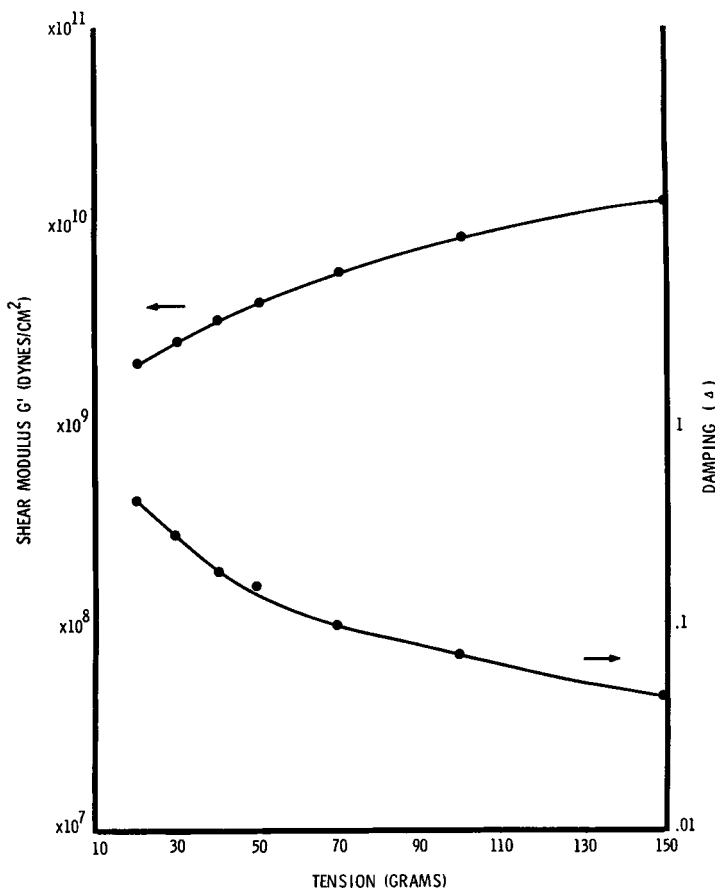


Fig. 2. The effect of tension on dynamic properties of films.

preciable decreases in chipping do not occur even at high loading. A pigment volume concentration of 47.3% is equal to 68.6% on a weight basis. There are very few plastics that can be loaded to almost 70% and still retain impact properties.

An interesting observation can be made from Figure 3. In both the modulus and damping curves, there are sharp breaks at 23.95 volume per-

TABLE IV
Comparison of Experimental and Industrial Alkyd Primers

Type	Bake	$G' \times 10^9$ dynes/cm ²	Δ	Impact
Industrial alkyd primer	30@400	3.68	0.154	5
Polyester modified	30@400	3.32	0.034	8
Polyether modified	30@400	2.83	0.035	6

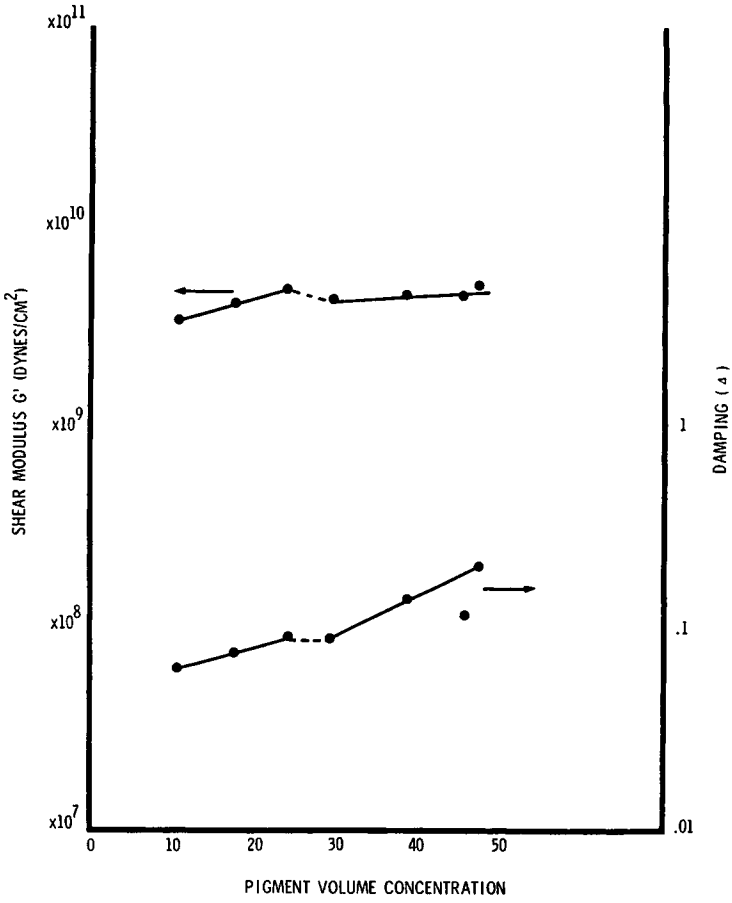


Fig. 3. The effect of pigment loading on dynamic properties of films.

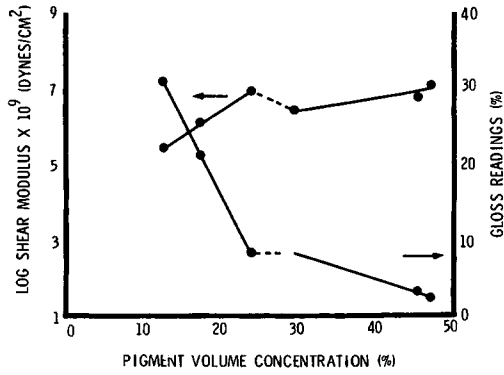


Fig. 4. Comparison of dynamic properties and gloss with pigment volume concentration.

cent. Asbeck and co-workers¹⁷ have shown that paint parameters, such as gloss, permeability and rusting, experience sharp breaks in their PVC curves. They attribute this to the critical pigment volume concentration (CPVC), or that point where there is sufficient resin present to fill completely the voids left between the pigment particles. This can be restated as, that point where the resin no longer surrounds the pigment but the pigment surrounds the resin. Figure 4 shows a comparison between gloss readings, dynamic properties and pigment volume concentration. Thus, dynamic testing can be used for determining the critical pigment volume concentration. Other methods that can be used for CPVC determination are permeability measurements and density measurements on unsupported films. For the system under consideration, the critical pigment volume concentration is 23.95%.

Varying the chemical composition of the primer has an effect on the dynamic properties of the film as well as on the impact properties. As the oil length, which is the percentage of fatty acid in the resin minus any water of esterification is increased, the shear modulus decreases and damping increases leading to a more flexible resin; one that has increased chip resistance. This is somewhat surprising since the cross-linking constituent is increasing and this should lead to embrittlement of the resin. However, it should be noted that the amount of phthalic anhydride drops from approximately 30 to 15%. Phthalic anhydride is the ingredient that adds stiffness to the polymer chains; thus, in this case, the loss of steric hindrance outweighs the extra cross-linking activity of the resin and flexibility increases.

In view of the preceding discussion, two experimental resins were prepared and pigmented to the same level as an industrial alkyd primer. Both resins are block copolymers; one a polyester, the other a polyether. The blocks have incorporated low glass transition temperatures into the polymer. This has been shown to increase impact resistance of polymers.⁴ The results indicate (Table IV) that both experimental resins have lower moduli and much lower damping than the industrial primer. The latter fact is surprising as it was expected that damping would increase as the glass transition temperature of the polymer was lowered. It is felt that this presently unexplained result will be better understood when a temperature capability is included in the mechanical testing of films.

References

1. T. J. Young and D. R. Hays, *Measurement of Chipping of Automotive Finishes*, S.A.E. Preprint No. 680-046.
2. R. M. Evans, H. R. Mara, and E. G. Bobalek, *Soc. Plastics Eng. J.*, **16**, 76 (1960).
3. E. G. Bobalek and R. M. Evans *Soc. Plastics Eng. J.*, **17**, 93 (1961).
4. S. Turley, *Organic Coatings and Plastics Preprints*, **27**, No. 2, 453-460 (1967).
5. P. I. Vincent, *Polymer*, **1**, 425 (1960).
6. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold Publishing Corp., New York, 1962.

7. U. Zorll, *Farbe Lack*, **73**, 200 (1967).
8. L. W. Chen and J. Kumanotani, *J. Appl. Polymer Sci.*, **9**, 3649 (1965).
9. J. Kumanotani, L. W. Chen, and T. Kuwata, *Bull. Chem. Soc. Japan*, **35**, 1341 (1962).
10. C. Hansen, *Off. Dig.*, **37**, 57 (1965).
11. P. Pierce and R. Holsworth, *J. Paint Tech.*, **38**, 263 (1966).
12. R. Roark, *Formulas for Stress and Strain*, McGraw-Hill Book Co., New York, 1954, p. 174.
13. C. White and R. Miller, unpublished results.
14. L. Nielsen, R. Wall, and P. Richmond, *SPE J.*, **11**, 22 (1955).
15. E. Kerner, *Proc. Phys. Soc. London*, **69B**, 808 (1956).
16. H. Thurn, *Kunststoffe*, **50**, 606 (1960).
17. W. Asbeck and M. Van Loo, *Ind. Eng. Chem.*, **41**, 1470 (1949); W. Asbeck, G. A. Scherer, and M. Van Loo, *Ind. Eng. Chem.*, **47**, 1472 (1955).

Received January 6, 1969

Revised April 17, 1969