

New Coating Materials Prepared by Radiation-Induced Polymerization. I. Mar-Resistant Coating Composition and Properties

H. OKUBO, M. KATO,* M. YOSHIDA, A. ITO, and I. KAETSU, *Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Gunma-ken, Japan*

Synopsis

A mar-resistant coating system was obtained by screening combinations of silicone and vinyl compounds. It was found that binary systems, such as the γ -glycidoxypropyltrimethoxysilane-glycidyl methacrylate system, were excellent not only in mar resistance but also in adhesion to base resin polymers. Haze values of these coatings, after the sand-falling test, reached less than 10%. The coating process consisted of three steps: the preparation of prepolymer, the coating to plastic surface, and the curing of the coating by heating. It was found that the prepolymerization step could be performed by irradiation very conveniently; the control of viscosity for coating application and thickness control could be possible without any gel formation. These coatings were also good in weather resistance due perhaps to the good adhesion to base resin and could be applicable to plastic spectacles, glazing materials, and a variety of other products.

INTRODUCTION

The authors have applied radiation-induced polymerization of glass-forming monomers at low temperatures to a casting process of organic glass materials¹ and found that the polymer articles having no optical strain could be obtained in a very short casting time. However, in general, organic glass materials do not perform satisfactorily in surface properties such as mar resistance or scratch resistance.

It was considered to be too difficult to obtain sufficient mar resistance in the base polymer. It is more desirable to limit the improvement to the surface of the base material only so as not to destroy the balance of various physical properties of the base resin. Consequently, coating is one of the best ways to improve the surface properties, and it is expected that radiation may be a useful means for preparing the coating.

Various tests have been done to find the most effective coating composition for the improvement of mar resistance on a polymer surface. However, most tests have not succeeded in satisfying the required level of mar resistance for practical use. For example, a number of single or multicomponent systems of vinyl monomers, including polyfunctional monomers, were tried.^{2,3} Silicone coatings proved to be superior to vinyl compounds in mar resistance.⁴⁻⁶

In this report, a new mar-resistant coating composition for organic glass surfaces and a method of preparation by radiation-induced polymerization are described.

* Present address: Tokyo Optical Company, Tokyo, Japan.

EXPERIMENTAL

A silicon coupling agent (product of Sinetsu Chemical Company), commercially available vinyl monomers, and a curing catalyst were used without special purification. Base resin was obtained by cutting the commercially available plastic sheet. That is, CR-39 resin, polycarbonate and poly(methyl methacrylate) sheets were obtained from the casting products of Tokyo Optical Company, Mitsubishi Gas Chemical Company and Mitsubishi Rayon Company, respectively. γ -Irradiation was carried out from a ^{60}Co -radiation source of 100,000 Ci, and the polymerization conversion was determined by weighing isolated polymer which was precipitated by ethyl ether. The viscosity of the polymerized solution (coating agent) was measured by a capillary viscometer. The polymerized solution was then coated on a plastic surface mainly by dipping or painting. The coated membrane was then cured by heating at 100°C. Curing by irradiation was also investigated using an EBG electron accelerator of 2.0 MeV energy.

The mar resistance was estimated by H value (haze value) following the sand falling test. A definite quantity of Soma sand was dropped during a determined time on the surface of a sample set in Gardner-type test equipment (Tokyo Seiki Co.) according to ASTM D 968-51. The H value of the tested sample was then measured by a haze meter (Nihon Seimitsu Kogaku Co., SEP-HS type) according to the following equation:

$$H(\%) = (Td/Tt) \times 100$$

where Td is the diffused light transmittance and Tt is the whole light transmittance. The H value is a variable based on the quantity of falling sand. The relationship is shown in Figure 1. A standard condition of 1380 g of Soma sand dropped for 10 sec was selected.

Pencil hardness was also determined as a measure of surface hardness according to JIS.K.5651. The friction coefficient was estimated, using Bowden-Leben-type friction coefficient measure equipment under a load of 500 g and a speed of 0.1 cm/sec.

The adhesion of the coating to the base resin was estimated by the cellophane tape cross-cut test at 25°C and 50% relative humidity.

The weather durability was tested by observing the changes in appearance, mar resistance, and adhesion after ultraviolet exposure at 63° ± 3°C by a xenon Weatherometer (Tokyo Rikakogyo Co., WE-6X-HC type).

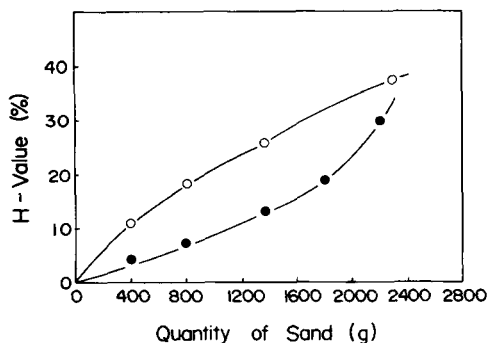


Fig. 1. Relationship between haze value and quantity of sand used in sand-falling test: (○) CR-39 base resin and (●) CR-39 resin coated with mar-resistant coating.

RESULTS AND DISCUSSION

Screening of Mar Resistance of Silicone-Vinyl Compound Coating Systems

Silicone polymer is superior in mar resistance because of its low friction coefficient, but is inferior in adhesion to other types of plastics. On the other hand, vinyl polymer is relatively good in adhesion but poor in mar resistance. The authors tried screening suitable combinations of silicone and vinyl compounds for the purpose of improving mar resistance and adhesion to organic glass materials. Results are shown in Figures 2 and 3. Excellent systems with regard to haze value, after the sand falling test, were as follows: KBM 303-GMA (KBM 303 50%-100%), KBM 403-GMA (KBM 403 20%-100%), KBM 403-KBM 303

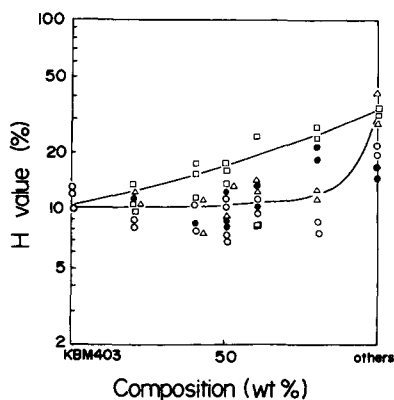


Fig. 2. Effect of composition on haze value in mar-resistant coating systems including γ -glycidoxypropyltrimethoxysilane (KBM 403): (O) KBM 403-KBE 1003 system, prepolymerization 3×10^6 R irradiation in the presence of 0.5% HClO_4 at 25°C; (□) KBM 403-KBC 1003 system, prepolymerization 3×10^6 R irradiation in the presence of 0.5% HClO_4 at 25°C; (Δ) KBM 403-GMA system, prepolymerization 8×10^4 R irradiation in the presence of 0.5% HClO_4 at 25°C; (●) KBM 403-KBM 303 system, prepolymerization heating at 55°C with 0.5% HClO_4 . KBE 1003 = Vinyltriethoxysilane; KBC 1003 = vinyltris(β -methoxyethoxysilane); GMA = glycidyl methacrylate; KBM 303 = β -(3,4-epoxycyclohexyl)ethyl trimethoxysilane; curing, 100°C 1 hr, then 60°C for 24 hr.

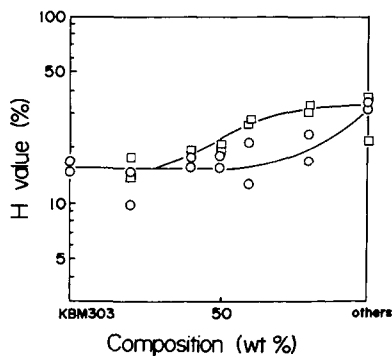


Fig. 3. Effect of composition on haze value in mar-resistant coating systems including β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane (KBM 303): (O) KBM 303-KBC 1003 system, prepolymerization 3×10^6 R irradiation in the presence of 0.5% HClO_4 at 25°C; (□) KBM 303-GMA system, prepolymerization 8×10^4 R irradiation in the presence of 0.5% HClO_4 at 25°C; curing, 100°C 1 hr, then 60°C for 24 hr.

(all compositions), KBM 403-KBC 1003 (KBM 403 40%–80%), KBM 403-KBE 1003 (KBM 403 20%–100%), and KBM 303-KBC 1003 (KBM 303 40%–100%), where KBM 303- β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, KBM 403- γ -glycidoxypropyltrimethoxysilane, GMA-glycidyl methacrylate, KBC 1003-vinyl tris(β -methoxyethoxy)silane, KBE 1003-vinyl trisethoxysilane.

These systems exhibited haze values of less than 20% and often reached values near 10%. In Table I, the haze values of various base polymer materials, after the sand falling test, are shown as a control for the results in Figures 2 and 3. CR-39 resin is the best base polymer in mar resistance among the organic glasses. However, its haze value is only about 25% according to Table I. On the other hand, the mar resistance of the silicone-vinyl binary systems in Figures 2 and 3 was far smaller than that of CR-39. The mar resistance increased with increasing silicone content as shown in Figures 2 and 3; thus, silicone-rich composition is more desirable for mar resistance. However, adhesion to base polymer resin was generally poor in extremely silicone-rich compositions. Moreover, important practical properties such as weather resistance and heat durability also depend on the adhesion between the base resin and the coating. These properties can be improved by increasing adhesion. It was found that the adhesion of coating to base resin was greatly increased by increasing the vinyl component in the silicone-vinyl binary system.

For example, the weather resistance of the KBM 403-GMA coating system could be improved by increasing the content of GMA as shown in Table II. The adhesion of this coating, however, differed with the type of base resin employed. For example, the adhesion of this coating to CR-39 resin was sufficient to pass the cross-cut test, but the adhesion to poly(methyl methacrylate) and polycarbonate was not sufficient even in the presence of GMA. It was concluded that an excellent balance of mar resistance and adhesion for practical use can be obtained by the combination of a silicone compound and a vinyl compound. These new coating materials are applicable not only to spectacle lenses, optical lenses, and other organic glass articles, but also to mirror and metal surfaces.

Preparation of Prepolymer for Suitable Coating by Means of Radiation-Induced Polymerization

The mar-resistant coating composition consisted of silicone and vinyl compounds. In order to complete the formation of the final film, it was necessary to complete both the vinyl polymerization of the vinyl compound and also the condensation type polymerization of the silicone compound. It was found that catalysts such as perchloric acid and trifluoroboron were effective for the polymerization of silicone compounds. On the other hand, initiation by heating with

TABLE I
Mar Resistance of Various Materials as a Control in Sand-Falling Test

Material	Haze value after sand-falling test, %
CR-39 Resin	25.6, 25.0
Poly(methyl methacrylate)	56.0, 56.9
Polycarbonate	61.2, 61.5
Inorganic glass	7.5, 9.6

TABLE II
Weather Durability of KBM 403-GMA Coating System at Various GMA Concentrations

GMA concentration, vol %	Weather durability after exposure to ultraviolet by xenon Weatherometer at 65°C		
	Crack formation	Release from base resin	Adhesion in cross-cut test after exposure of 500 hr ^a
0	after 130-160 hr of exposure	after 500 hr of exposure	0/100 (100/100)
3	after 280 hr of exposure	no release after 500 hr of exposure	100/100 (100/100)
5	after 470 hr of exposure	no release after 500 hr of exposure	100/100 (100/100)
10	no crack after 500 hr of exposure	no release after 500 hr of exposure	100/100 (100/100)
20	no crack after 500 hr of exposure	no release after 500 hr of exposure	100/100 (100/100)

^a Values in parentheses are values before the weathering test.

peroxide catalysts and irradiation by γ -ray were effective for the polymerization of vinyl compounds. Further, it was found that a certain viscosity was necessary for effective coating on the material surface. The viscosity of monomeric systems consisting of silicone and vinyl compounds was below 10 cP, which was too low to prevent dripping of the coating solution. It was found that a viscosity of 50-200 cP was suitable in order to coat easily and homogeneously with the proper film thickness.

Consequently, the prepolymerization of monomeric solutions was investigated as a viscosity-controlling process. It was found that radical prepolymerization of vinyl compounds suited the purpose, because vinyl polymerization gave the linear polymer required to increase the viscosity. Polymerization of silicone compound at elevated temperature caused gel formation easily and led to increased viscosity very quickly owing to the formation of a three-dimensional polymer structure. The polymerization of vinyl compound was possible by radical initiators such as BPO. However, catalytic polymerization usually needs relatively high temperatures. In catalytic polymerization, the viscosity of the coating system often increases very rapidly with increase in conversion owing to the acceleration effect of the polymerization rate by the polymerization heat. In other words, polymerization conditions suitable for viscosity control were very narrow in catalytic polymerization, while in the case of radiation polymerization, polymerization conditions over a very large range could be used to obtain the desired viscosity. This advantage was remarkable, especially in the presence of the curing catalyst for silicone components. The curing catalyst was usually added at the initial stage of prepolymerization and resulted in gelation or excess viscosity increases at elevated temperatures due to the silicone polymerization.

Radiation-induced polymerization was best for controlling the viscosity of prepolymers. The relationship between irradiation and viscosity is shown in Figures 4-6. According to the results in Figure 4, viscosity reached about 50-100

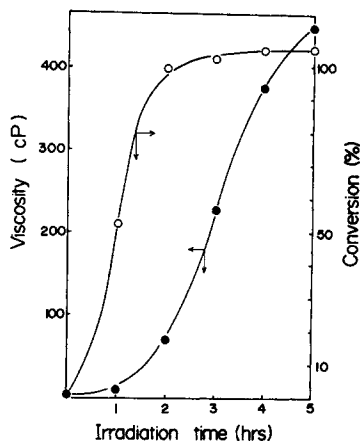


Fig. 4. Relationship between conversion, viscosity, and irradiation time in the prepolymerization of KBM 403-GMA system: composition, KBM 403 75 vol-%-GMA 25 vol-% with 0.7% HClO_4 ; and dose rate, 5×10^5 R/hr, at 25°C , in air.

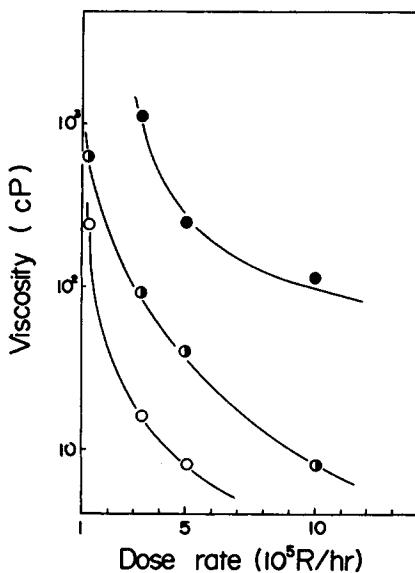


Fig. 5. Effect of dose rate on the viscosity of prepolymer in the prepolymerization of KBM 403-GMA system: irradiation dose, 2×10^6 R, at 25°C , in air; (●) KBM 403 75 vol-%-GMA 25 vol-%; (◐) KBM 403 80 vol-%-GMA 20 vol-%; (○) KBM 403 85 vol-%-GMA 15 vol-%; HClO_4 , 0.7%.

cP at 100% conversion, then increased to more than 400 cP with time owing to the initiation of silicone polymerization. However, it was obvious that viscosity control was carried out easily by varying the irradiation conditions, such as dose and dose rate.

The prepolymer was coated on the base resin surface and then cured by heating to complete the polymerization of the silicone component. A highly crosslinked structure of coated polymer was necessary to give excellent mar resistance and complete adhesion. Heating at temperatures greater than 60°C was necessary for this purpose.

Curing by irradiation and the combination of irradiation and catalytic method

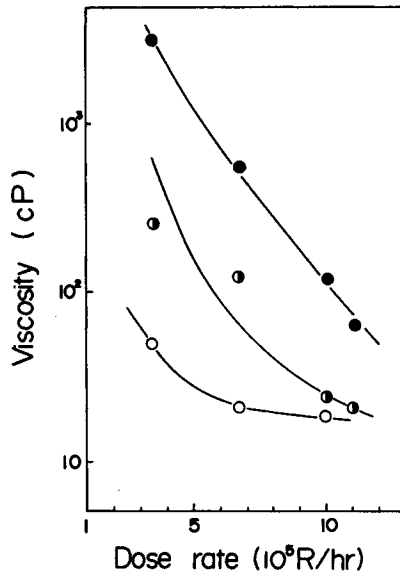


Fig. 6. Effect of dose rate on the viscosity of prepolymer in the prepolymerization of KBM 403-GMA system: irradiation dose, 4×10^6 R, at 25°C , in air; (●) KBM 403 75 vol-%-GMA 25 vol-%; (◐) KBM 403 80 vol-%-GMA 20 vol-%; (○) KBM 403 85 vol-%-GMA 15 vol-%; HClO_4 , 0.7%.

was also tried for comparison. These results were shown in Table III. Simple irradiation curing was not sufficient for excellent mar resistance, but further increase in haze value was observed by irradiation after catalytic curing. An increase in adhesion to affect mar resistance can be expected by the irradiation of the coating to form chemical bonding between the coated polymer and the base resin polymer.

Thus, the coating process consists of three steps: preparation of prepolymer of vinyl monomer by irradiation; coating of prepolymer on the base resin; and curing of the coating by heating to complete the polymerization of the silicone compound.

Relationship Between Viscosity, Thickness, and Mar Resistance of the Coating

The relationship between the viscosity of the prepolymer, the thickness of the coating, and the mar resistance is shown in Figures 7 and 8. These three factors are closely related to each other. The thickness of the coating increases with an increase in viscosity, as seen in Figure 7. The mar resistance of the coating is affected directly by the thickness of the coating. That is, haze value after the sand falling test increases with an increase in coating thickness below about 5μ and then becomes constant with further increase in thickness. However, as the uniformity of the coating decreased with increase in viscosity and thickness, the suitable thickness was in the range of $5\text{--}40 \mu$. From these results, it is obvious that viscosity control in prepolymerization is important.

The dipping method was mainly used for the coating in this experiment, but other methods can also be used. For example, dipping is suitable for articles of moderate size such as spectacles and small lenses, while the spraying method

TABLE III
Effect of Irradiation on Curing of Coated Prepolymer in Relation to Mar Resistance of KBM 403-GMA System^a

Run no.	Composition, vol-%		Curing condition		Haze value after sand-falling test, %
	KBM 403	GMA	Heating	Irradiation	
1	50	50	none	1×10^7 R, 25°C	20.1
2	40	60	none	1×10^7 R, 25°C	22.4
3	20	80	none	1×10^7 R, 25°C	24.7
4	50	50	100°C, 1 hr	none	15.1 (1 μ thick)
5	50	50	100°C, 1 hr	none	12.4 (2 μ thick)
6	50	50	100°C, 1 hr	none	13.1 (2 μ thick)
7	50	50	100°C, 1 hr	none	10.4 (5 μ thick)
8	50	50	100°C, 1 hr (run 4)	7×10^5 R, 25°C after heating	12.4 (1 μ thick)
9	50	50	100°C, 1 hr (run 5)	7×10^5 R, 25°C after heating	11.8 (2 μ thick)
10	50	50	100°C, 1 hr (run 6)	7×10^5 R, 25°C after heating	10.0 (2 μ thick)
11	50	50	100°C, 1 hr (run 7)	7×10^5 R, 25°C after heating	9.1 (5 μ thick)

^a Irradiation was carried out by Resonance Transformer Electron Accelerator (2 MeV, 6 mA) in this experiment.

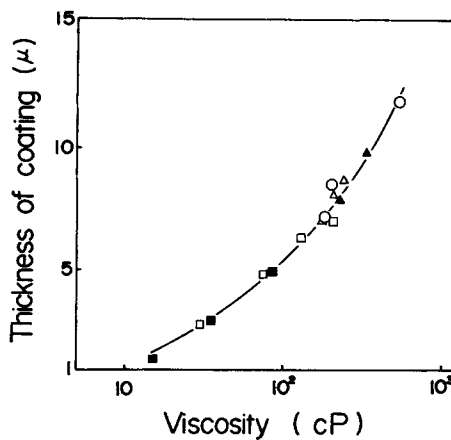


Fig. 7. Relationship between viscosity of prepolymer and thickness of coating film in KBM 403-GMA system: (□) KBM 403 80 vol-%-GMA 20 vol-%; (■) KBM 403 85 vol-%-GMA 15 vol-%; (▲) KBM 403 90 vol-%-GMA 10 vol-%; (Δ) KBM 403 93 vol-%-GMA 7 vol-%; (○) KBM 403 95 vol-%-gma 5 vol-%; HClO₄, 0.7%. Prepolymerization, irradiation total dose, 2×10^6 R; dose rate, 5×10^5 R/hr, at 25°C, in air; curing, 100°C 1 hr, then 60°C for 24 hr.

is applicable for relatively large articles such as sheet, plate, and other glazing materials. Painting and rolling methods are also useable. The relationship between viscosity and the thickness was obvious from the results of the dipping method.

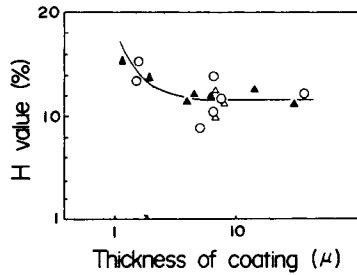


Fig. 8. Relationship between coating thickness and haze value after sand-falling test in KBM 403-GMA system: (\blacktriangle) KBM 403 90 vol-%-GMA 10 vol-%; (\triangle) KBM 403 93 vol-%-GMA 7 vol-%; (\circ) KBM 403 95 vol-%-GMA 5 vol-%; HClO_4 , 0.7%. Prepolymerization, irradiation total dose, 2×10^6 R; dose rate, 5×10^5 R/hr at 25°C , in air; curing, 100°C 1 hr, then 60°C for 24 hr.

Relationship Between Mar Resistance, Pencil Hardness, and Friction Coefficient

The excellent mar resistance of the present coating can be attributed to the low friction coefficient of the silicone component. In Figure 9, the relationship between the friction coefficient of the coating and the monomer composition in various mar-resistant systems is shown. The relationship between the friction coefficient and haze value is shown in Figure 10.

The friction coefficient was further plotted against the pencil hardness to demonstrate the relationship of mar resistance and surface hardness as shown in Figure 11. From these results, a definite relationship could be recognized between friction coefficient and mar resistance. However, the friction coefficient did not show good agreement with pencil hardness, though some agreement was observed within the same series of coating system. This fact suggests that mar resistance is essentially a different property from surface hardness such as pencil hardness. Mar resistance or scratch resistance is probably more closely related to surface smoothness or slipping property than to simple surface hardness measured by pulling or penetrating with a needle or sharp rod.

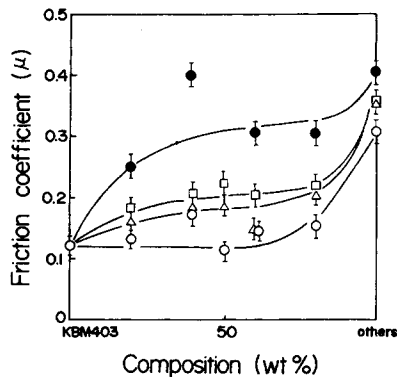


Fig. 9. Relationship between friction coefficient of coating and composition in KBM 403-including systems: (\bullet) KBM 403-KBM 503 system, prepolymerization 3×10^6 R irradiation in the presence of 0.5% HClO_4 ; (\circ) KBM 403-KBE 1003 system, prepolymerization 3×10^6 R irradiation in the presence of 0.5% HClO_4 ; (\square) KBM 403-GMA system, prepolymerization 8×10^4 R irradiation in the presence of 0.5% HClO_4 ; (\triangle) KBM 403-KBC 1003 system, prepolymerization 3×10^6 R irradiation in the presence of 0.5% HClO_4 ; curing, 100°C 1 hr, then 60°C for 24 hr. KBM 503 = γ -Methacryloxypropyltrimethoxysilane.

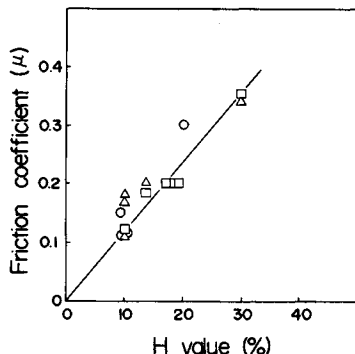


Fig. 10. Relationship between friction coefficient and haze value after sand-falling test of mar-resistant coating systems: (O) KBM 403 80 vol-%-KBE 1003 20 vol-%, (\square) KBM 403 80 vol-%-KBC 1003 20 vol-%, and (Δ) KBM 403 80 vol-%-GMA 20 vol-%. Prepolymerization, 3×10^6 R irradiation in the presence of 0.5% HClO_4 ; curing, 100°C 1 hr, then 60°C for 24 hr.

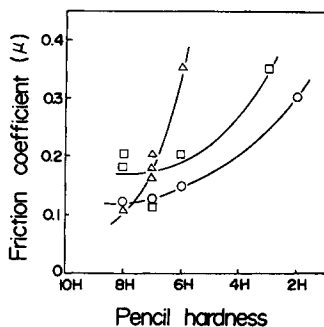


Fig. 11. Relationship between friction coefficient and pencil hardness of mar-resistant coating systems: (O) KBM 403 80 vol-%-KBE 1003 20-vol-%; (\square) KBM 403 80 vol-%-KBC 1003 20-vol-%; (Δ) KBM 403 80 vol-%-GMA 20 vol-%. Prepolymerization, 3×10^6 R irradiation in the presence of 0.5% HClO_4 ; curing, 100°C 1 hr, then 60°C for 24 hr.

Silicone and fluorine compounds are known to have small friction coefficients, and no doubt one of the best ways to improve the mar resistance is to modify the plastic surface principally by silicone and fluorine compounds. However, there are many difficult problems related to the utilization of such low-friction materials: the coating, homogeneous mixing and reactions with other components, improvement in adhesion, etc. The radiation technique can be convenient and useful in solving these problems.

References

1. I. Kaetsu, F. Yoshii, H. Okubo, and A. Ito, *Appl. Polym. Symp.*, **26**, 165 (1975).
2. Irving E. Muskat, et al. (to Pittsburgh Plate Glass Co.), U.S. Pat. 2,332,461., Oct. 19, 1944.
3. Edwin H. Cloaker (to Rohm & Haas), Jpn. Pat. 35-17847., Dec. 6, 1960.
4. Alfred J. Burzynski, et al. (to Owens Illinois), U.S. Pat. 3,451,838., June 24, 1969.
5. Eugene H. Engelhardt (to du Pont), U.S. Pat. 3,390,203., Jun. 25, 1968.
6. Eugene H. Engelhardt, et al. (to du Pont), U.S. Pat. 3,476,827., Nov. 4, 1969.

Received July 28, 1976

Revised December 13, 1976