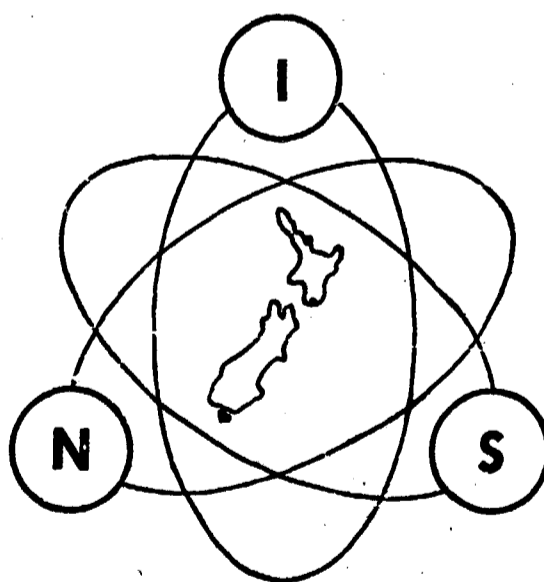# RADIATION CURING OF SURFACE COATINGS

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RADIATION CURING OF SURFACE COATINGS

A PRELIMINARY EXPERIMENTAL STUDY

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INTRODUCTION

The use of beams of high energy electrons for the rapid curing of especially formulated surface coatings is a new technique of considerable potential value in New Zealand industry. The resins or other binding materials used for this purpose must be capable of curing by a free radical chain process similar to that occurring in the polymerisation of monomers to form solid plastics. Two such substances are - (a) unsaturated polyester resins dissolved in styrene, and (b) acrylic monomers. Both of these polymerise on irradiation to form a solid cross-linked material with no residual solvent. Detailed information on the process is scarce (see reference 1 for recent publications) and usually confined to the industrial concern sponsoring the research. Several patents on particular aspects have been issued, notably to the Ford Motor Company in America.

In order to gain experience of this technique, some experimental trials were conducted in September 1970 using the electron beam from the Van de Graaff accelerator at the Institute of Nuclear Sciences. This machine accelerates electrons up to 3 million volts energy and fires them into air through a thin aluminium window. The resultant beam has much greater range ($\frac{1}{2}$" or more in plastics) than is needed to penetrate and cure a paint film of a few mils thickness, but in this research machine it is limited to small currents. To simulate the radiation intensities needed for rapid curing, the beam was confined to a circle of $\frac{1}{2}$" diameter. One object of this preliminary trial was to assess the suitability of this facility for subsequent industrial research. A second was an evaluation of the radiation curing of commonly available unsaturated polyester resins in styrene manufactured by A.C. Hatrick (N.Z.) Ltd and kindly made available for this

purpose. A third arose from discussions with Mr N.A. Price, Mr A.H. Gollop, Mr R. McCapra and other members of the printing trade who pointed out the need for a rapid curing or drying process to speed up the rate of lithographic printing. Various pigments were mixed with polyester resin - styrene solutions and tested for their suitability as radiation curable inks.

This first trial was simple and brief, intended mainly to assess the need and feasibility of more sophisticated further research.

METHODS

(1) Polyester Resins

Polyite 8009 resin supplied by A.C. Hatrick (N.Z.) Ltd was spread on small tinned steel plates in films of 8-thousandths-of-an-inch thickness. This is a high reactivity (readily cured) unsaturated resin made from maleic acid, phthallic anhydride and propylene glycol, and dissolved in styrene to form a viscous liquid containing 66% resin solids. 10% by volume of a 10% solution of wax in styrene was added to some samples. Each sample was irradiated in air with 2 MeV (million electron volt) electrons through a $\frac{1}{2}$" diameter aperture in a $^1/4$" aluminium plate a few minutes after spreading, and was examined subsequently for surface tack (finger touch), colour and water spotting. Irradiation doses were determined from (a) current density measurements (1 $\mu a/cm^2$ = 0.18 Mrads/sec surface dose[5]) and (b) colour changes induced in 1mm thick strips of "HX" perspex, previously calibrated with ^{60}Co gamma radiation. The two agree within 5% for specimens appreciably thinner than the electron range.

Radiation doses are measured in Mrads (megarads). This is a unit of energy absorbed per gram of irradiated substance, and 1 Mrad corresponds to the absorption of 10^8 ergs per gram.

(2) Resin-Pigment Mixtures

Mixtures of 8009 (high reactivity) and 8001 (low reactivity) Polylite

resins with the pigments listed below were prepared by the staff of Coates Bros with a laboratory rolling mill. Sufficient pigment was added to increase the viscosity of the resin-styrene solution from initially 5 to 10 poises to 70-80 poises which is typical of that needed for lithographic inks. Wax solution in styrene was added in some cases. Samples were spread with a silk screen on tinned metal plates to 2/1000" thickness, and were irradiated in air 1 to 5 minutes afterwards. They were tested for surface tack (finger touch), and hardness by rubbing as an indication of cure below the surface by Mr D.W. Dunn of Coates Bros, immediately after irradiation.

Pigments

Designation	Type	% added to resin
Chrome	206 Scarlet Chrome (Lead Chromate)	45
Yellow	410 Benzidene Yellow	20
Green	40 PMTA Emerald Green (Phthalocyanine)	20
Black	400 Channel Dense Black (Carbon)	15

RESULTS

Unirradiated clear resins in styrene remained stable and viscous after spreading for weeks. Those containing pigments were stable in bulk but tended to harden slowly on the surface after spreading and would be unsuitable as lithographic inks for this reason. Tables 1 and 2 summarise the response of these preparations to radiation. The fully radiation cured products were hard and somewhat brittle, and the cured inks especially adhered only poorly to their metal backing. The "curing doses" listed are those needed for complete loss of surface tack without regard to hardness. No discolouration of any of the pigmented resins was observed but the thick layers used would make this difficult to detect.

TABLE 1 - Polylite 8009 Resins, 66% Solids in Styrene

No.	Wax %	Dose Mrads	Dose Rate Mrads/sec	Surface Teck immed.	Surface Teck 4 days	Water Spot - 4 days 1 hr exp	Water Spot - 4 days 48 hrs exp	Colour	Curing Dose Mrads	Curing Time secs irradn.
1	1	2.5	0.35	cons.	sl.	clear	clear	normal)		
2	1	5	"	sl..	v.sl.	clear	clear	")	18	51
3	1	10	"	v.sl.	none	sl.haze	sl.haze	")		
4	1	18	"	none	none	v.sl.	haze	crazed, yellow)		
5	0	2.5	"	cons.	cons.	haze	clear	normal)		
6	0	5	"	sl.	v.sl.	haze	clear	")	10	28
7	0	10	"	none	none	sl.haze	haze	")		
8	0	18	"	none	none	sl.haze	haze	yellow)		
9	1	5	3.5	v.cons.	v.cons.	clear	clear	normal)		
10	1	10	"	cons.	cons.	sl.haze	clear	")	>20	> 7
11	1	20	"	sl.	sl.	clear	clear	")		
12	1	1.5	7	v.cons.	v.cons.	clear	clear	")		
13	1	2.7	"		v.cons.		clear	")		
14	1	5.5	"		cons.		clear	")		

4.

TABLE 2 - Polylite Resins + Pigments

No.	Resin	Wax %	Pigment	Dose Mrads	Dose Rate Mrads/sec	Surface Tack	Hardness	Curing Dose Mrads	Curing Time secs Irradn
1	8009	1	chrome	1.2	0.35	v.sl.	soft		
2	"	1	"	2.5	"	none	fair	2.5	7
3	"	1	"	5	"	none	hard		
4	"	1	"	10	"	none	hard		
5	"	1	"	5	3.5	sl.	soft	> 5	> 1.4
6	"	0	yellow	5	0.35	v.sl.			
7	"	0	"	10	"	none	hard	10	28
8	"	1	"	5	"	v.sl.			
9	"	1	"	10	"	v.sl.	fair	20?	56?
10	8001	1	"	10	"	v.sl.			
11	"	1	"	20	"	none	hard	20	56
12	"	0	"	5	"	none			
13	"	0	"	10	"	v.sl.		20?	56?
14	8009	0	green	2.5	"	v.sl.		5	14
15	"	0	"	5	"	none			
16	8001	0	"	5	"	v.sl.			
17	"	0	"	10	"	none	hard	10	28
18	8009	1	black	0.6	"	v.sl.	sl.soft)		
19	"	1	"	1.2	"	v.v.sl.	"	2.5	7
20	"	1	"	2.5	"	none	hard		
21	"	1	"	5	"	none	hard		
22	"	1	"	1	5.0	v.v.sl.			
23	"	1	"	1.9	"	none	hard	1.9	0.4
24	"	1	"	3.8	"	none	sl.soft)		
25	8001	0	"	2.5	0.35	none	hard	2.5	7
26	"	0	"	5	"	none	hard		

CONCLUSIONS

(1) The dose needed for curing increases with increasing dose rate. This confirms similar trends reported in available literature[2,3] and implies that there may be a lower limit to the curing time regardless of increases in radiation intensity made possible by newly developed electron accelerators. It is therefore essential to make tests at the dose rates and other time scales envisaged for ultimate industrial use.

(2) The addition of pigments to polylite resins either had little effect on the dose needed for curing (yellow and green), or reduced this dose (chrome and black). The latter effect was unexpected. Carbon black not only increases radiation sensitivity but appears to have removed the dose rate effect noted in (1). Such effects could obviously be of great value and warrant further studies.

(3) The reactivity of the resin (maleic to phthallic ratio) and the addition of wax made very little difference to the curing dose, though wax appeared to increase this slightly. Wax is commonly added to prevent access of oxygen from surrounding air and therefore reduce air inhibition at the surface.[3] This should result in improved water spot resistance but no such effect was observed in these trials. In fact, no completely cured resin gave a satisfactory water spot test. Possibly the time after spreading was insufficient to allow an effective wax film to form before irradiation.

(4) <u>Suitability of experimental facilities.</u>

Particularly because of (1) above, any industrial tests must involve high dose rates. Table 3 summarises the facilities available with the Institute's accelerator in comparison with those of a typical industrial machine. Future possibilities are also listed but must be regarded as guesses. A summary of the process characteristics of presently available industrial accelerators is given by Davison[4].

TABLE 3 - Electron Accelerator Characteristics

Machine	Voltage millions	Total current ma	Irradiated Area cm²	sq.in.	Fraction of Beam over Irradiated Area	Dose Rate Mrads/sec
(1) Van de Graaff at I.N.S., filament source as used Sept. 1970, rarely available. Usual operation	2	0.01	1.3	0.2	0.25	0.35
Maximum - Sept. 1970 (a)	2	0.2	1.3	0.2	0.25	7 -
or (b)	2	0.1	0.15	0.023	0.15	18
Possible future max. (a)	2.5	0.4	1.0	0.15	0.25	18
or (b)	2.5	0.2	0.25	0.039	0.25	36
(2) Ditto, but normal gas source with instant conversion, frequently available. Usual maximum	2	0.05	1.3	0.2	0.25	1.7
Possible future maximum	2	0.15	1.3	0.2	0.25	5
(3) Typical industrial accelerator, 50 ma beam scanned over 36", spread in 4" of air to 2" width.	0.4	50	460	72 (36×2)	1.0	20
Future accelerators						100?

7.

The main limitations of our existing facilities are -

(a) "Industrial" dose rates can be obtained only over areas less than a quarter of a square inch. Tests on these are obviously difficult, partly because of uncured resins surrounding the treated area. New testing techniques could improve this situation but only partially.

(b) At present, irradiations must be done one at a time with "warm up" periods of about 1 minute for the filament source and 5 minutes for instant conversion. These delays after spreading and before irradiation would not occur with a continuous belt industrial machine, and may have important effects. The time required for formation of a wax film is a case in point. Some form of narrow continuous belt or remote controlled spreading device inside the shielded target room is needed to overcome this.

(c) The likely influence of atmospheric oxygen as an inhibitor of curing needs investigation. Present techniques of spreading and irradiation do not permit the exclusion of oxygen, and must be changed to allow this.

(5) Future Work.

Considerable research will be needed to modify resin-pigment mixtures for use as radiation curable inks. Other coatings for industrial applications requiring a more tough and pliable film, such as on metal cans, also need development, possibly based on acrylic monomers. Provided specialist staff are available then some progress towards this can be made with the facilities already existing at the Institute, but a satisfactory trial under industrial conditions requires an industrial accelerator.

REFERENCES

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2. A.S. Hoffman and D.E. Smith, Mod. Plastics, 1966, 43, 111.

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4. W.H.T. Davison, J.O.C.C.A. 1969, 52, 946.

5. M.J. Berger and S.M. Seltzer (N.A.S.A. SP-3012, 1964) give the stopping power of lucite (perspex) for 2 MeV electrons as 1.8 MeV per thickness of 1 g/cm^2 and this figure is nearly independent of the atomic composition of the stopping material and of electron energy down to 0.7 MeV. The energy dissipated in the stopping material in any thin layer near the surface (i.e., at thicknesses much less than the electron range) when exposed to an electron current of 1 $\mu a/cm^2$ is thus 1.8 MeV cm^2/g × 1.0 $\mu a/cm^2$ or 1.8 × 10^7 ergs/g/sec. Since 1 rad = 100 ergs/g this corresponds to 0.18 Mrads/sec.