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Dup
APPLIED SCIENCE RESEARCH LABORATORY
UNIVERSITY OF CINCINNATI
CINCINNATI 21, OHIO

PROGRESS REPORT NO. 5
August 1, 1952 - September 30, 1952

ON

DEVELOPMENT OF NEW POLYMERS FOR AIRCRAFT APPLICATION
Navy Bu Aer Contract NOa(s) 52-090 c

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Summary

A. Chloroprene-Methacrylic Acid Copolymers.

1. Cornell Tests and Curing Studies.

Highly encouraging results have been obtained from the ninth series of rain-erosion specimens tested at Cornell. Progress now has been made from an impractical heat-cure, giving results inferior to both the Goodyear and Gates topcoats, to an air-cure system superior to Gates and nearly equal to Goodyear. The best coating of this last series employed an air-cure, with Goodyear accelerator 983-C and diaminodiphenylmethane (DADPM) as the curing agents. This sample (9 I, Table I) eroded through in one spot in 60 minutes and was tested a total time of 80 minutes.

Specimens 9F and 9E using accelerator 983-C alone gave times of 40-70 and 30-50 respectively. All panels cured with ZnO displayed poor rain erosion resistance. Thus, the addition of 2 parts ZnO to the curing system which gave the 60-80 minute performance resulted in a specimen with times of 20 and 50 minutes.

A comparison of panels containing carbon black with non-carbon black specimens revealed that in both instances the non-carbon black panel showed greater resistance to erosion.

Effect of Carbon Black on Rain-Erosion Resistance ¹					
Cornell Test No.	Carbon Black	Curing System	Curing Conditions	Time to erode thru coating	Total Test Time
9E	None	Accel 985-C	Room Temperature	30	50
9F	None	Accel 983-C	Room Temperature	40	70
9C	2 pts. Royal Spectra	Accel 983-C	Room Temperature	10	50
9B	None	10 pts. Zimate / 2 pts. DADPM	1 hour at 120 C.	30	50
8K	1 pt. EPC black	"	1 hour at 120 C.	20	30

1 Copolymer AK-20 was used in all panels.

Complete results of the ninth series of rain-erosion specimens are shown in Table I. Laboratory tests of other curing systems are listed in Table II. In view of the deleterious effects of ZnO as demonstrated in the last Cornell series, no further work on ZnO cures is planned.

2. Creep Behavior of the C-MA Copolymers.

The results of the latest rain erosion test have been compared with the creep behavior of the coatings under test (Progress Report No. 4, Fig. II). No obvious correlation is apparent. Low compliance, which is exhibited by Goodyear's and Gates' materials does not seem to be of importance. For instance, specimen F, which had one of the highest compliances, lasted 40 minutes, which is better than results shown by "low compliance" specimens. The results indicate that zinc oxide, as a curing agent is detrimental to rain erosion performance, even though it lowers the compliance of a given coating. Effects of pigmentation, fillers etc., seem to overshadow

the importance of viscoelastic properties. Further creep study will be confined to organic curing agents which give homogeneous lacquer coatings. During the last period, the study of the C-MA copolymer creep behavior was continued. Zinc oxide, being the most promising curing agent at the time was given special attention. On aging, the films containing 5 parts zinc oxide (Figure I) showed a continually decreasing compliance. At the same time a small decrease in tensile and elongation was observed. This gradual decrease in compliance was also experienced with the C-MA gumstock on aging. Figure II shows the variation of compliance for varying the amount of zinc oxide from 0 to 10 parts. As expected the increase of zinc oxide decreases the compliance.

3. Effect of Water on C-MA Lacquers

Cornell Aeronautical Laboratory has reported that the University of Cincinnati rain erosion specimens exhibit bubbling during the rain erosion tests. To get some insight in the origin of this bubbling, most of the previously tested Cornell specimens were immersed in 30 C water for 24 hours and the effects noted.

In several instances bubbles were formed. Sufficiently large bubbles yielded water when broken with a pin. The bubbling was specially obvious in the eight rain erosion series where most of the specimens contained silica in addition to 10 parts Ethyl Zinate and 4 parts DADPM as a curing agent. Generally, the specimens giving the best rain erosion results of the eight series were found to be least attacked by water. In the earlier series, where the main curing agent had been magnesia, fewer cases of bubbling were noted.

Possible blistering on water immersion is not the only reason for C-MA film failure, however. Thus, metal oxide cures have shown little or no blistering on water immersion, yet (as evident from the last Cornell series) can have very marked effects on film durability. It has been observed previously that, with metal oxides, dispersed particles in the lacquer film can be detected under a 50X microscope. It is reasonable to believe that such spots also may be loci of rain erosion attack. Before these water sensitivity tests can be properly evaluated, the investigation of other curing agents will be necessary.

4. Outdoor Exposure of the C-MA Lacquers

Eight C-MA copolymer coated 3S-aluminum panels were subjected to outdoor exposure for eleven months (November, 1951 to October, 1952). This experiment was run to determine the effect on the adhesion between the finish system and the pretreated aluminum surface. The 3" x 6" specimens were placed vertically facing south on top of the physics Building of the University of Cincinnati.

These specimens appeared to show satisfactory overall resistance to weathering. Adhesion was found satisfactory with all specimens. The topcoat had retained its generally rubbery characteristics, but had lost a part of its original elasticity. All specimens had lost their original gloss indicating some surface deterioration.

On immersion of the specimens in 30°C water for 24 hours, some blistering was noted where the aluminum surface had been

treated with Alodine 100. When the lacquer was applied to a freshly ground surface, the specimen did not exhibit any blistering. Turco W01 and Alodine 600 treated specimens showed less blistering than the ones treated with Alodine 100.

B. Chloroprene-Methacrylamide Copolymers

The investigation of curing variables has been continued for the chloroprene-methacrylamide copolymer. Experiments varying the time and temperature during the bake for the 6 parts Zimate, 2 parts magnesia and 2 parts sulfur cure have shown that one, two and three hours at 120°C all give comparable cures. In all three cases, 2 weeks conditioning after bake were required to attain a tensile strength of 4000 psi or better. Similar results can be attained at 100°C curing temperature by baking for 8 hours. Several different accelerators and accelerator combinations have also been examined but none compare favorably with the 6,2,2 Zimate, magnesia, sulfur cure.

Air cure studies have been conducted with a number of curing agents. None of these gave tensile values equal to those of the high temperature cures. However, Goodyear accelerator 983-C provided a fairly satisfactory air cure showing a tensile strength of 3400 psi after 20 days.

Compounding studies were conducted with carbon blacks using the 6,2,2 Zimate, magnesia, sulfur cure. Both Royal Spectra and EPC blacks decreased the tensile strength compared to the control without materially affecting either the elongation or set. Ludox silica, precipitated and milled into the polymer before solution, gave test data comparable to the control.

Chloroprene-methacrylamide lacquers have been examined for age stability, both with and without curing system. No deterioration of the lacquer stored without curing agents has been detected after a month of aging. Even with the curing system added the lacquer is reasonably stable up to a week's storage.

Polymer mixtures of chloroprene and methacrylamide have been prepared for study both by milling and grafting. Polymethacrylamide and polychloroprene are incompatible with milling. However, grafted copolymers of methacrylamide and chloroprene have been prepared. These are similar to the copolymers in appearance and properties. However, compositions and conversions are difficult to control and reproduce.

Primer studies have shown that the Bostik primer provides the most suitable undercoat system for the chloroprene-methacrylamide copolymer. Several coats of Bostik Tiecoat also appear advisable to insure a smooth finish.

Program

A. C-MA Copolymers

In view of the excellent results secured with diamine-Goodyear 983-C curing systems, other proportions of DADPM, as well as other diamines will be evaluated for their capacity to impart rain-erosion resistance to C-MA copolymer. The possibility of employing paraffin as a protection against water penetration will be studied both in C-MA and Goodyear formulations. Investigation of polyhydroxy aromatics as candidate cures is to be pursued. All work will be restricted to

the service practical air-cures. Possible improvement of the commercially available Goodyear and Gates lacquers will be investigated; the new polymer, du Pont's Hypalon, will be included in our next rain-erosion tests. Creep studies of the various C-MA coatings will be continued, and the degree of water sensitivity will be determined for possible correlation with film failure.

B. Chloroprene-Methacrylamide Copolymers

Cornell panels will be prepared from the chloroprene-methacrylamide lacquers using the Bostik undercoat system. Curing studies will be continued. In view of indications that the Goodyear accelerator 983-C is essentially pyrocatechol, other polyhydroxy aromatic compounds will be included in these studies.

Experimental

A. Curing of C-MA Copolymers

Further study of air-cure versus heat cures of MgO demonstrated the superiority, in-so-far as tensile strength is concerned, of the room temperature cure. After 17 days, the air-cured film possessed a tensile strength nearly 500 p.s.i. greater than that exhibited by the heat-treated films. All films were poured from the same lacquer solution, eliminating the possibility of any significant variation in formulation.

Air-Cure versus Heat-Cure of MgO² Cured Films

	<u>After 3 days</u>	<u>10 days</u>	<u>17 days</u>
Air Cure	3500 p.s.i.	6300	6910
1 hour at 120° C.	5640	6400	6440

2. 1 pt. MgO employed as cure with copolymer AK-20.

Other curing systems investigated are summarized in Table II. Much of this work was concerned with zinc oxide formulations which have given outstanding tensile values. However, in view of the recent rain-erosion results no further work on the zinc oxide cures is contemplated.

B. Preparation of C-MA Outdoor Exposure Specimens

(Results reported under "Summary")

The C-MA copolymer lacquers were applied to 3 x 6" 3 S aluminum panels. Prior to the C-MA primer application, the aluminum surface was treated in the following ways: ground, Turco W0 I, Alodine 100 and Alodine 600. The grinding of the aluminum surface was done with three-m-ite elek-tro-cut cloth No. 320, while in Turco W0 I and Alodine washes, manufacturer's instructions were followed. The primer was applied by flow method and subsequently cured (5% MgCO₃ as agent) for 4 hours at 120° C. Two similar C-MA copolymer topcoats (ca 55% conversion 13% acid) were cast from a mixture of cyclohexanone and methyl isobutyl ketone (80:20 by volume) as solvent. Topcoats were cured with 1 part magnesia and baked for 2 hours at 120° C.

C. Chloroprene-Methacrylamide Copolymers

The best physical properties have been obtained with chloroprene-methacrylamide by curing with 6 parts Zimate, 2 parts magnesia, and 2 parts sulfur with a bake of 2 hours at 120° C. This cure has now been investigated further at other times and temperatures as follows:

Table III

Effect of Time and Temperature of Cure on Tensile Strength

Temp.	Time hrs	Tensile Strength, psi, at the following times after cure	2 days	3 days	5 days	6 days	7 days	8 days	14 days
120	1	3520			3560		3740		3990
	2	3610			3560		3420		4050
	3	3630			3600		3230		4080
100	2		2260			2800		3020	
	5		2980			3110		3650	
	8		3490			3960		4070	

All three cures at 120° C. appear comparable. At 100° C a bake of 8 hrs was necessary to achieve similar results.

Some miscellaneous accelerators were also tested. The condensation product of formaldehyde and para cresol (DMPC) was prepared and tested as a cross-linking agent for the amide groups. In all cases results were lower than the 6-2-2 control. Previously formaldehyde had also shown no success. All cures were baked 2 hrs at 120° C.

Table IV

Miscellaneous Curing Agents with Chloroprene-Methacrylamide Copolymers

<u>Agent</u>	<u>Days after Cure</u>	<u>T.S. psi</u>	<u>Elong.%</u>	<u>Set</u>
2 MgO - 3 ZnO	7	3240	1130	10
4 MgO - 5 ZnO	7	3240	1020	11
9 DMPC	17	2850		
9 DMPC - 622	17	3000		
9 DMPC - 2 MgO	17	2770		
622 (Control)	14	4050		

The success experienced with air curing of C-MA lacquers suggested the investigation of air cures with the chloroprene methacrylamide polymers. Highest results were obtained with Goodyear accelerator 983 C; none of the results were outstanding, however. Apparently chloroprene-methacrylamide polymers do not cure as readily as C-MA; no instances of lacquer thickening with magnesia have ever been observed with chloroprene-methacrylamide polymers.

Table V

Chloroprene-Methacrylamide Air Cures

<u>Agent</u>	<u>Days After Cure</u>	<u>Tensile Strength psi.</u>
6-2-2	10	1900
	20	2470
	38	1950
4 MgO; 5 ZnO	13	2480
	25	2290

Table V (Cont'd)

Agent	Days After Cure	Tensile Strength psi.
5 ZnO	10	2570
	20	2650
5 MgO	10	2800
	20	2900
	44	2750
Goodyear 983 C 0.9 cc/gm	10	2600
	20	3420
	38	2990
5 ZnO - 983 c 0.9cc/gm	13	2240
	25	2270

The effects of carbon black and silica were tested on chloroprene-methacrylamide copolymers with the 6-2-2 cure (Zimate-magnesia-sulfur). Tensile strengths for both royal spectra and EPC blacks were lower than the control; silica had no adverse affect. All films were baked 2 hrs. at 120° C.

Table VI

Effect of Carbon Black and Silica upon Physical Properties

Material	Parts	Days after Cure	T.S. psi.	Elong. %	Set
Control		7	4180	1000	10
EPC	2	5	2850	950	10
	5	5	2670	930	12
	10	5	3030	940	10
	20	5	3020	920	12
Royal	2	7	2890	950	7
	5	7	2980	1030	8
	10	7	3030	970	12
	20	7	3280	900	21
SiO ₂	2	7	4100	950	5
	5	7	4250	930	11

Lacquer stability has been studied for the purpose of checking shelf life of the lacquer without curing agents and also to determine the behavior of the lacquer with curing agents added. The 6-2-2 cure (Zimate-magnesia-sulfur) was used throughout with a bake of 2 hrs. at 120° C.

No change in free film physical properties was noted after a month's shelf storage for the lacquer solution. Curing agents were added at the time of test. Results on the fresh polymer solution were 3300 psi tensile strength, 800 % elongation at break, and 8% permanent set; corresponding results on the month old lacquer were 3870 psi, 940%, and 6%. Further aging tests on this sample are anticipated.

The lacquer with curing system added also showed reasonable stability; at the end of one week there was a slight decrease in viscosity with a settling out of a small amount of gelled polymer. However, the physical properties of the film poured from the liquid portion were not impaired.

Table VII

Lacquer Stability with Curing System Added

<u>Age</u>	<u>Viscosity, sec.</u>	<u>T.S.psi.</u>	<u>Elong.%</u>	<u>Set</u>	<u>Days Film Aged</u>
Fresh	10.6	3610			2
		3560			5
		3420			7
		4050	1000	7	14
2 days	10.6	3840	860	7	7
7 days	9.0	4180	1010	10	7

Fractional precipitation experiments have indicated that the chloroprene-methacrylamide copolymer is heterogeneous in nature, with most of the methacrylamide polymerizing after the chloroprene is already polymerized. For this reason, polymer blending and grafting experiments have been undertaken to see if a polymer having the same properties as the copolymer can be achieved by these means. No success was encountered by blending: polymethacrylamide and polychloroprene proved to be incompatible. Grafted polymers were successfully prepared, however. Chloroprene was polymerized by itself in a typical emulsion recipe for 5 hours at 30°. The monomeric chloroprene was then stripped off, methacrylamide added with more initiator and polymerization continued. Shortstopping, coagulation, and washing were conducted in the usual manner. The cure was 2 hrs at 120° C. with 6-2-2 Zimate-magnesia-sulfur.

Table VIII

Grafted Copolymers of Methacrylamide and Chloroprene

<u>Conversion, %</u>	<u>% Chloroprene</u>	<u>T.S. psi.</u>	<u>Elong, %</u>	<u>ASTM Set</u>
48	92	4240	890	7½
48	95	3970		

These polymers were very similar in appearance and physical properties to copolymers prepared by the usual procedures. This would indicate that the copolymers are largely polychloroprene grafted with polymethacrylamide. Production by grafting techniques appears to show less promise, however, as it affords less accurate control of composition and conversion.

Table I

Cornell Series No. 9

Specimen No.	Polymer No.	Additives	Curing Agents	Primer	Time to erode through coating	Total Time of test
9A	A-37 ¹	2 pts Royal Spectra Carbon Black	5 pts ZnO	Bostik	20 min.	50 min.
9B	AK-20 ²	None	10 pts Zimate ³ + 2 pts DADPM ⁴	C-MA	30 min.	50 min.
9C	AK-20	2 pts Royal Spectra	2 mls. Accel 983-C ⁵ per 2 gms polymer	C-MA	10 min.	50 min.
9D	AK-20	None	5 pts ZnO	Bostik	Film began to peel off in layers after 10 min.	50 min.
9E	AK-20	None	2 mls Accel. 983-C per 2 gms Polymer	Bostik	30 min.	50 min.
9F	AK-20	None	2 mls Accel. 983-C per 2 gms Polymer	C-MA	40 min.	70 min.
9G	AK-20	5 pts Hydrophobic Silica	5 pts ZnO	Bostik	20 min.	50 min.
9H	AK-20	None	1 pt MgO	C-MA	20 min.	60 min.
9I	AK-20	None	2 mls 983-C/2 gm Polymer + 4 pts DADPM	Bostik	60 min.	80 min.
9J	AK-20	None	2 mls 983-C/2gm poly-mer + 4 pts DADPM + 2 pts ZnO	Bostik	20 min.	50 min.

For footnotes see next page

Table I (Cont'd)

1. C-MA Copolymer with conversion of 55.0% and acid content of 12.7%.
2. C-MA Copolymer with conversion of 52.5% and acid content of 11.8%.
3. Zinc diethyl dithiocarbamate.
4. p-p'-Diaminodiphenylmethane.
5. Goodyear Accelerator 983-C.
6. 9B cured at 120° C. for 1 hour, All others room temperature cures.

Table II

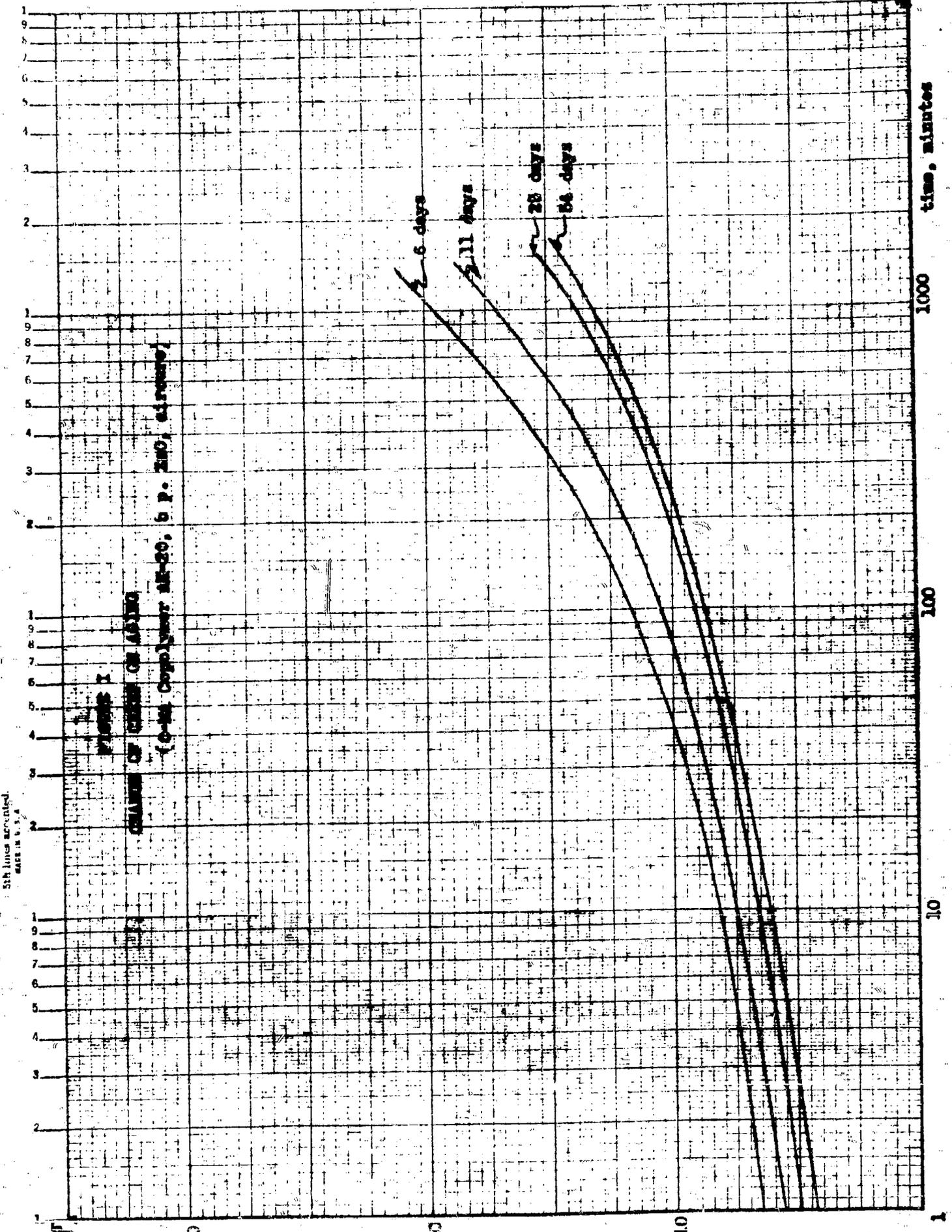
Additional Air-Cure Systems (10 days) Employed with C-MA²

<u>Curing System</u>	<u>Tensile (psi)</u>	<u>% Elongation at break</u>	<u>Permanent Set ASTM</u>	<u>1 min. Recovery</u>
6 pts DADPM	2930	1050	49	2½
6 pts DADPM 1 pt ZnO	4330	875	39	3
8 pts DADPM	2350	1080	45	4½
6 pts DADPM 2 pts ZnO	5790	820	25	4
4 pts DADPM 1 pt ZnO	4000	900	33	3½
2 pts DADPM 1 pt ZnO	3700	850	25	2½
1.5 ml 983-C 8 pts DADPM	2400	-	-	-
1 pt ZnO	3660	850	27	2
2 pts ZnO	5900	-	-	-
3 pts ZnO	5800	-	-	-
4 pts ZnO	7100	-	-	-

2. Copolymer AK-20 with conversion of 52.5% and acid content of 11.7%.

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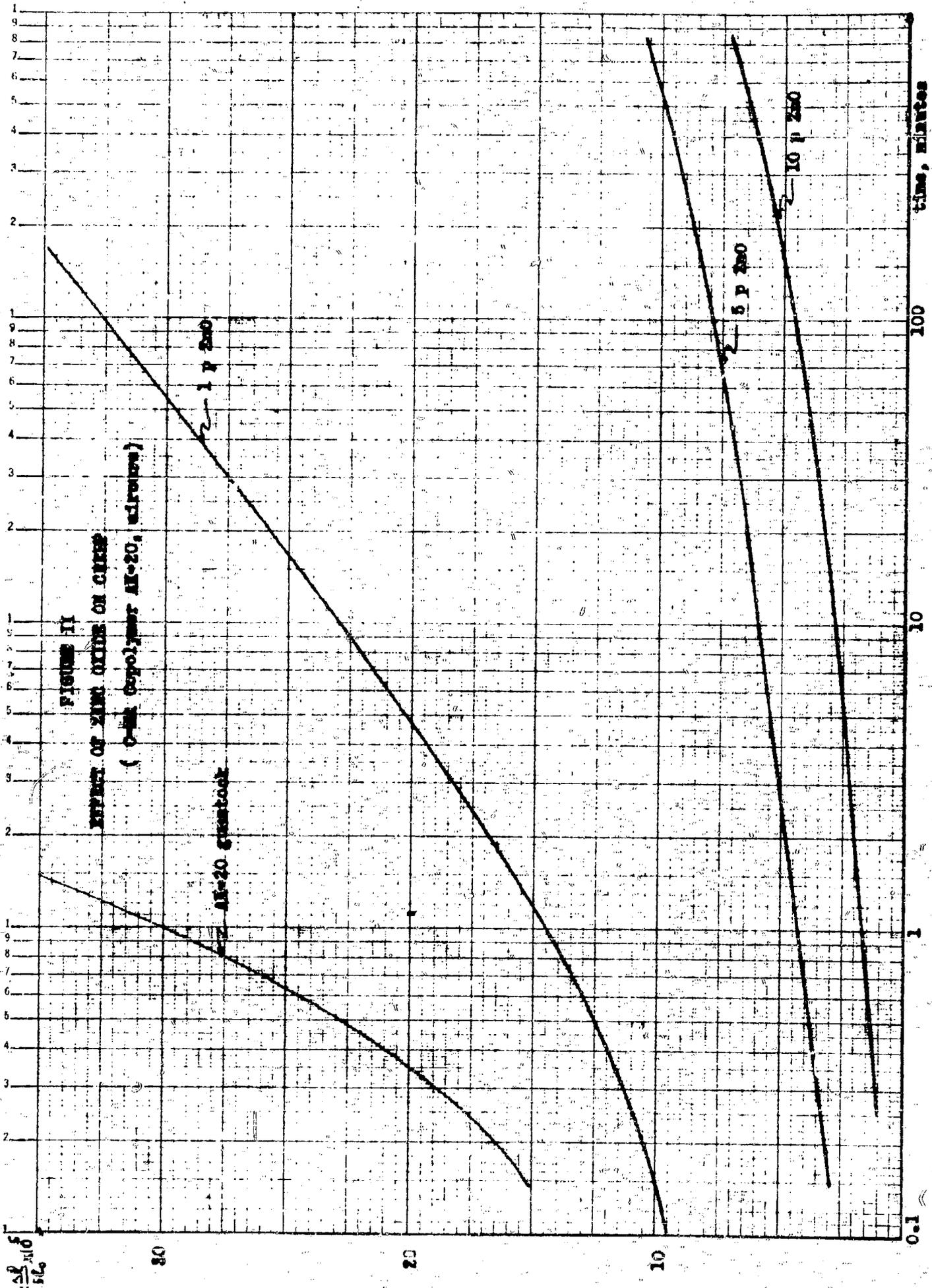
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