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VANADIUM TRINEODECANOATE PROMOTER FOR FIBERGLASS-POLYESTER SOIL--ETC(U)

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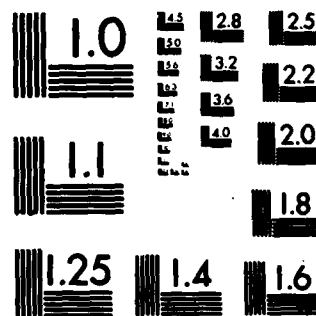
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# **Vanadium Trioxide Promoter for Fiberglass-Polyester Soil Surfacing**

by

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JUNE 1960

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## FOREWORD

The program was authorized by Marine Corps RDT&E Work Directive No. 00079, Program Element 63765M, and was carried out between April 1979 and March 1980. This is a final report describing the synthesis and testing of a vanadium trimethacrylate solution to be used in a promoter for a fiberglass-reinforced plastic soil surfacing material.

This report was reviewed for technical accuracy by Dr. Eugene C. Martin.

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(U) A Marine Corps chemical formulation developed for the construction of fiberglass-reinforced plastic surfaces for soils consists of a polyester resin, cumene hydroperoxide catalyst and a promoter solution containing a vanadium salt and N,N-dimethyl-p-toluidine. A new, relatively simple method for preparing the vanadium trineodecanoate (VND) solution has been devised to replace the previously used commercial salt solution which is no longer being manufactured. This preparation is now ready to be scaled-up to pilot plant size. Reactivity and accelerated aging studies indicate that the VND solution functions at least as well as the commercial salt. Laminates made under either dry or wet conditions with the VND displayed significantly higher flexural strengths than those made with the commercial material.

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## INTRODUCTION

A requirement of the Marine Corps is the ability to upgrade soil surfaces to withstand vehicular and aircraft traffic. This requirement has been fulfilled by the Civil Engineering Laboratory (CEL), Port Hueneme,<sup>1,2</sup> with the development of a fiberglass-reinforced plastic (FRP) system. The system is comprised of a fiberglass matting which is spread on the ground, then sprayed with a catalyzed polyester resin which cures to form a tough flexible surface.

The polymer system consists of a polyester resin, a peroxide catalyst (cumene hydroperoxide) and a two-part, premixed, promoter solution. The promoter specified consists of N,N-dimethyl-p-toluidine (DMT) and a vanadium compound marketed as Vanadium Ten-Cem by Mooney Chemicals, Inc. The discontinued production of Vanadium Ten-Cem was responsible for initiating this program to prepare and evaluate a replacement for the Mooney Chemicals product.

Guidelines set forth for the substitute vanadium solution were as follows:

1. The reactivity must be similar to that of the Ten-Cem.
2. The properties of the FRP must be as good as those obtained when Ten-Cem is used in the formulation.
3. The shelf life should be equal to, or better than, that of Ten-Cem (although the shelf life of Ten-Cem has never been determined); the desired value is 5 years.
4. The synthesis of the vanadium compound should be adaptable to a large-scale operation which can be completely defined using materials and equipment readily available in the United States.

In addition, for the sake of convenience and accuracy in field use, the ratio of catalyst to promoter solution should be maintained at a simple whole number, preferably the 4:1 ratio currently used for the promoter containing Ten-Cem.<sup>1</sup>

At the start of this program the ratio of Ten-Cem to DMT was 1.34:1 by weight; however, this ratio is inconvenient for field use. Thus, an investigation of a more convenient formulation was included in this study.



## EXPERIMENTAL

Some of the items used in this program were furnished by CEL. These included the polyester resin RS 50338 (PPG Industries, Inc.), DMT (technical grade, R.S.A. Corp.), cumene hydroperoxide (Thalco Corp.), a small amount of Vanadium Ten-Cem, and the fiberglass mat Fabmat C-4020 (Fiberglass Industries).

### TEN-CEM

The ingredients in Ten-Cem include vanadium trineodecanoate (VND), a phosphorus-containing constituent, and xylene solvent. The amount of vanadium in the solution is approximately 3%. In the particular sample of Ten-Cem that was available to us, there was a sizable amount of black precipitate which was probably a product of decomposition formed after standing for a long period of time.

### SYNTHESIS OF VANADIUM TRINEODECANOATE

The more important reagents used in the attempted synthesis of a replacement VND are as follows:

Neodecanoic acid (NDA) -- prime grade and technical grade, Exxon Chemical Company.

Vanadium trioxide ( $V_2O_3$ ) -- reagent grade, Alfa Products, Ventron, Inc.

Vanadium pentoxide ( $V_2O_5$ ) -- reagent grade, J. T. Baker Chemical Company; technical grade, Matheson Coleman and Bell.

Triethyl phosphate -- practical grade, Matheson Coleman and Bell.

### REACTIONS USING VARIOUS REAGENTS

To synthesize a replacement VND a number of reactions using various reagents and various reaction conditions were investigated as follows:

1. Sodium neodecanoate (0.03 molar) + vanadyl sulfate (0.01 molar). Mixing aqueous solutions gave a dark material which was extractable in xylene. Overnight, the dark material precipitated out of solution.

2.  $V_2O_3$  (0.01 mole), NDA (0.04 mole), p-xylene sulfonic acid (0.02 mole), 25 ml xylene. After refluxing overnight with stirring, the theoretical amount of water was obtained from the system; black, xylene-insoluble material formed. Upon evaporating the xylene, a viscous liquid formed which solidified upon standing and which was only partially xylene-soluble after 2 months.

3.  $V_2O_3$  (0.01 mole), NDA (0.04 mole), benzene phosphonic acid, 25 ml xylene. Reaction run as in 2.; only 20 to 25% of theoretical water was recovered. The olive-green xylene layer contained largely NDA.

4.  $V_2O_3$  (0.01 mole), NDA (0.06 mole), triethyl phosphate (0.035 mole). Heated with stirring in air for 22 hours at 173-177°C. Solution contained 4.0% vanadium ion; 22% of the unreacted oxide was recovered.

5. Vanadium (III) acetylacetonate (0.02 mole), NDA (0.06 mole), triethyl phosphate (0.07 mole). Heated with stirring at 140-155°C for 2 hours. Removed the volatile reaction product at 25 torr and 60-90°C, then removed last fraction at 1-2 torr and 90°C. Some of the acid and triethyl phosphate were also distilled. Dark olive-green solution contained 3.5% vanadium. After evaporating, a complete dissolution of the oil was obtained. Some material separated on standing.

6. Vanadium (III) acetylacetonate (0.04 mole), NDA (0.12 mole), triethyl phosphate (0.06 mole). Heated 159-161°C under dry nitrogen with stirring for 3 hours (3.5 hour warm-up period), distilled reaction product (2,4-pentadione). Resulting product was dissolved in equal weight of xylene and stored under nitrogen.

7.  $V_2O_3$  (0.01 mole), conc. HCl 18 ml, NDA (0.06 mole), xylene (70 ml), paraformaldehyde (0.2 g) under  $N_2$ .  $V_2O_3$  was dissolved in HCl with mild heating. NDA and other reagents added and the system heated until reflux was achieved (much HCl evolved during the heating). Water azeotrope was removed; reaction appeared complete after about 3 hours, but reflux was continued for about 3 more hours. Green xylene-soluble solution resulted with a small quantity of insoluble material. Viscosity of reaction solution was high.

8.  $V_2O_3$  (0.01 mole), conc. HCl (18 ml), NDA (0.066 mole), xylene (70 ml), paraformaldehyde (0.2 g) under  $N_2$ . Conducted in similar fashion to 7. with similar results.

9.  $V_2O_3$  (0.01 mole), conc. HCl (18 ml), NDA (0.066 mole), triethyl phosphate (0.07 mole), xylene (70 ml) under  $N_2$ . Conducted in similar fashion to 7. and 8., green solution was produced having much reduced viscosity compared to 7. and 8. Solution was stable under nitrogen. In the presence of air, formation of black, insoluble sludge was noticed. In reactions 7., 8., and 9. loss of xylene during reaction occurred, and xylene had to be added to the system.  $V^{+3}$  concentration in the 7., 8., and 9. cases was much lower than expected on the basis of assumption of complete reaction. In performing the gel time tests, the promoter when added to the resin, seemed to have a thread-like or polymeric appearance.

10.  $V_2O_3$  (0.01 mole), 15 ml conc. HCl, NDA (0.063 mole), triethyl phosphate (0.035 mole), paraformaldehyde (0.22 g), xylene (25 ml) under  $N_2$ . This reaction was conducted with much more control of the temperature and reaction conditions than 7., 8., and 9. The oxide was dissolved by gradual addition of the oxide to the HCl at 80-90°C under nitrogen. The remainder of the components were then added to the system and vigorously stirred as the aqueous phase was removed in 2-1/2 hours by azeotropic distillation. The green solution was then filtered through Celite.

11.  $V_2O_5$  (0.01 mole), NDA (0.06 mole), 95% hydrazine (0.015 mole),  $H_2O$  (0.05 mole), 25 ml xylene.  $V_2O_5$  was added to the solution of the other components and heated to 60°C under air. Reaction began immediately on addition. Temperature was increased to 160-170°C and water removed azeotropically by refluxing overnight. Xylene-insoluble material was removed and the xylene evaporated to dryness. The viscous dark-green oil (5.7% V) remained which gelled at room temperature after 3 days and was no longer soluble in xylene.

12.  $V_2O_5$  (0.01 mole), NDA (0.06 mole), 95% hydrazine (0.015 mole),  $H_2O$  (0.05 mole), 25 ml xylene. This reaction was conducted in a fashion similar to 11., except that the heating time was reduced to 5 hours. The resulting oil gelled on standing. After 16 days only 25% was soluble in xylene.

13. Reaction 11. under  $N_2$ . This reaction was conducted as 12., except that xylene was not stripped from the solution. Some gel formed after 3 days at 25°C.

14.  $V_2O_5$  (0.01 mole), conc. HCl (15 ml), 1.4 g 90% formic acid, NDA (0.063 mole), triethyl phosphate (0.035 mole), paraformaldehyde (0.2 g) xylene (25 ml). This reaction was conducted by dissolving the oxide in HCl with stirring under nitrogen, then effecting the reduction with formic acid. The system was heated for 2 hours at 70-80°C. The remainder of the reaction was conducted according to reaction 10.

Reaction 14. worked quite well and this procedure was scaled-up by a factor of 30 successfully. A more detailed procedure is given in Appendix A. Several variations of the procedure were made such as using technical grade  $V_2O_5$ ; this variation did not alter the product noticeably. No problem was encountered when technical grade NDA was used, except that more of the material was required to make up for the lower acid content. When the triethyl phosphate was added at a later time than given in the procedure, a gel was obtained. Addition of trimethyl phosphate instead of triethyl phosphate at the normal time resulted in solidification of the reaction mixture. Thus, the given procedure must be followed closely. Final concentration of the vanadium salt can be varied considerably by altering the amount of xylene added.

## ANALYSIS OF VANADIUM IN VND SOLUTIONS

The method of analysis is based on a method given in reference 3. The detailed procedure is given in Appendix B.

## MEASUREMENT OF GEL TIME AND TIME TO MAXIMUM TEMPERATURE

The reactivities of the VND solution in the polymer system were determined by measuring the gel times under controlled conditions. The method was somewhat different from that given in reference 2 because the same gel timer was not available. The gel times in this work were measured with a Tecam gelation timer and required a sample size of approximately 100 g, considerably larger than that used by Dow.

The amount of cumene hydroperoxide remained fixed for all of the gel time measurements at 1.1 phr. This amount was chosen from Figure 5 of reference 1 as giving a gel time of about 10 minutes which is approximately the desired value. At the beginning of the program a promoter solution was prepared containing Ten-Cem and DMT in a ratio of 1.34:1 by weight (1.2:1 by volume). This promoter solution was used for all of the testing done with Ten-Cem. For much of the preliminary testing of new vanadium salt solutions, the VND and DMT were added to the resin separately. Occasionally, a difference in gel times was noted when premixed promoter solution versus the separate ingredients was used.

The time to maximum temperature was also measured in a simultaneous, but separate, measurement in the gel test. The actual maximum temperature was not measured since it is a function of thermal contact, sample size, and sample configuration. Temperatures of over 200°C were often obtained and the resulting polymer samples were highly fractured. The time to maximum temperature was usually about 1.6 to 1.8 times larger than the gel time. The detailed procedure is given in Appendix C.

## HARDNESS OF POLYMER SAMPLES

The hardness of each of the polymer samples obtained in the gel time experiments was measured with a Barcol Hardness Tester. Since the polymers were highly fractured, reliable values were difficult to obtain. The hardness values found in this study did not vary appreciably for any of the polymers reported here. The only samples for which significantly lower hardness values were obtained were for polymers which required a very long time to cure.

## COMPOSITE PREPARATION

Two-ply laminates were prepared by a procedure similar to that given in reference 2 for the purpose of providing samples for flexural strength testing. The laminates were either 15 x 23 cm (6 x 9 in.) or 23 x 30 cm (9 x 12 in.). One layer of Fabmat C-4020 was laid on a large sheet of

Mylar film (woven side down). This was covered with catalyzed polymer solution and rolled with a laminating roller to get rid of air bubbles. A second layer of the fiberglass mat was then put in place and the process was repeated. In most cases the polymer in the first layer had not gelled when the second layer was added; this had no apparent effect on the flexural strength. The amount of polymer added was that amount which would be 60% of the total weight of the laminate. This usually resulted in a laminate containing about 55% resin. Mixing of the resin was done in the same manner as that used for the gel time measurements.

Some composites were prepared in the presence of water. In this case the fiberglass mats were soaked in water, allowed to drain for about a minute, then weighed and laid on the Mylar film. Under these conditions the mats were saturated with water. The resin was then poured on and rolled as before. The laminates made under wet conditions were milky white in appearance in contrast to the usual transparent yellow-brown color of the polymer cured under dry conditions.

#### FLEXURAL STRENGTH DETERMINATION

Flexural strengths of the laminates were measured according to ASTM D790-71 using a 3-point bending apparatus in an Instron testing machine. Strips for the measurements were approximately 13 mm wide x 127 mm long x 6 mm thick (0.5 in. x 5 in. x 0.25 in.), and the supports were 86 mm (3.4 in.) apart. The strips were always tested with the woven side of the mat down. Either 5 or 6 samples from each laminate were used in determining the strength value.

#### RESULTS AND DISCUSSION

Gel time testing was carried out with the vanadium salt solution obtained from several of the reactions listed in the Experimental section. An attempt was made to adjust the amount of vanadium salt added to be the same in every case as when adding Ten-Cem. However, very little or only marginal success was achieved until the product from reaction 14. was tested. A comparison between this material and Ten-Cem is shown in Table 1. It can be seen that the gel time and time to maximum temperature for the new VND solution is about twice that obtained for Ten-Cem. When the reaction was scaled up by a factor of 30, the results were essentially the same.

TABLE 1. Comparison of Ten-Cem With New VND Solutions.

VND soln.	Gel time (min.)	Time to max. temp. (min.)	Barcol hardness
Ten-Cem	6.8 (avg. of 10)	13.3	48.5
Ten-Cem + 2 g water	3.5	6	45
14	12.25	20	46
14 + 2 g water	4.5	8.5	42
14, scaled-up	14.1 (avg. of 2)	23.4	45

It was also of interest to compare how these materials would behave in the presence of water. Thus, before addition of the promoter, 2 g of water were added to the polyester resin and well mixed. The large decrease in gel times and times to maximum temperature, shown in Table 1, were unexpected since Dow<sup>2</sup> reported essentially no change in gel time and an increase in time to maximum temperature. The reason for the decrease is probably due to the fact that the catalyst and promoter set up some sort of a redox reaction which is greatly enhanced by the presence of water. There was no significant change in the Barcol hardness.

Accelerated aging studies at 60°C were initiated using this new vanadium salt solution. Since it is desirable to be able to premix the DMT and VND solutions prior to use, aging studies were carried out on both the promoter solution and VND solution. Solutions were stored under air and under nitrogen to determine whether air oxidation had a significant effect on reactivity. The solutions used in the aging tests were as follows:

- a. Promoter solution containing VND and DMT in ratio of 1.34:1 by weight under air. (This ratio is the same as that used with the Ten-Cem.)
- b. Similar promoter solution under nitrogen.
- c. VND solution under air.
- d. VND solution under nitrogen.
- e. Promoter solution similar to a. except stored at ambient temperature.

Table 2 shows the results of the aging studies. Samples were removed periodically from some of the solutions for gel time determinations. Not all of the solutions were tested each time; for example, there appeared to be no reason to check solution d. for most of the time since the results for solution c. did not change very significantly.

It can be seen that most of the solutions appear to produce an increase in gel times for the first week or two and then level off.

On comparing the results for solutions a. and b., it can be seen that there is some effect due to air oxidation. When stored under nitrogen, there is essentially no change in the reactivity over the whole 175 day period. At 60°C, 175 days is calculated to be equivalent to storage for 5.5 years at 25°C. It must be recognized that there is quite a bit of scatter in the data, some of which may be attributed to changes in ambient test conditions.

TABLE 2. Aging of Vanadium Trineodecanoate Solutions.

Solution	Age (days)	Gel time (min.)	Time to max. temp. (min.)	Barcol hardness
a. Promoter soln.* 60°C under air	0	12.75	21	44
	0	15.5	25.75	45
	7	25	40.75	48
	14	32.25	54.25	49
	21	24	37.75	49
	32	31	51.75	48
	45	38.25	66.75	50
	56	35	57.75	51
	65	45.5	79.5	49
	78	35.5	59.5	47
	101	32.25	54.75	49
	149	24.25	40.75	49
	175	47.25	89	49
b. Promoter soln.* 60°C under nitrogen	0	14.1	23.4	44
	14	21.5	35.5	51
	21	20.75	33.25	49
	32	23.25	38.25	48
	45	24.25	39	51
	56	23.5	37	49
	65	17.25	27	46
	78	21.25	34	48
	101	20.75	33.75	47
	149	15.5	25.25	48
	175	19.5	31.75	50

TABLE 2. Aging of Vanadium Trineodecanoate Solutions. (Cont'd)

Solution	Age (days)	Gel time (min.)	Time to max. temp. (min.)	Barcol hardness
c. Vanadium	0	14.1	23.4	44
neodecanoate	14	16.75	28	51
soln.**	45	17.5	28.25	52
60°C under air	56	21.25	32.75	50
	65	22	34.5	49
	78	26	42.75	46
	101	22	36.25	48
	149	19.5	31.25	46
	175	29	48	50
d. Vanadium	0	14.1	23.4	44
neodecanoate	149	12.25	19.5	47
soln.**	175	19	30.75	50
60°C under nitrogen				
e. Promoter	0	14.1	23.4	44
soln.*	7	19	30.75	50
ambient temp.	14	24	38.5	48
under air	21	21.75	35.25	46
	32	29.25	48.5	52
	45	25.25	39.5	51
	56	28.5	45.5	49
	65	23.5	36.5	50
	78	28.5	46.5	48
	101	34	56.75	47
	149	21	33.5	49
	175	33.75	56.5	47

\* Vanadium neodecanoate to DMT ratio = 1.34 to 1.0.

\*\* DMT (not aged at 60°C) added for gel time determination.

DMT has a deleterious effect on the VND reactivity when stored under air (compare data for solutions a. and c.). When stored under nitrogen there is very little effect of the DMT. The promoter solution stored under air at ambient temperature gives gel times intermediate between a. and b. Similar observations were made in regard to the formation of a precipitate in the solutions. Solution a. first had a precipitate after 21 days. At the end of the study, a. and e. had large amounts of precipitate, b. still had only a small amount, and c. and d. had virtually no precipitate.



It can be concluded from this study that there is no storage problem with the new VND solutions. However, the promoter solution, containing both VND and DMT, will undergo some change unless stored under nitrogen. The formation of a precipitate does not appear to be a problem in regard to reactivity but could be a problem if hose lines or valves become clogged.

At this time, it was decided to investigate a promoter solution consisting of VND and DMT in a 1:1 ratio and also to look at ratios of catalyst to promoter of 2:1 and 3:1, in addition to the usual 4:1. Because of the results obtained in the first aging study, only a single promoter solution was used. It was stored under air at 60°C. The ratio of 1:1 can be either by volume or by weight since the densities of these two liquids are approximately the same (0.935 g/cc for DMT and 0.954 g/cc for the 3% VND).

Table 3 gives the results for the three concentrations of promoter solution. The ratios 4:1, 3:1, and 2:1 correspond to amounts of promoter added of 0.28, 0.37, and 0.55 phr, respectively. Changing the VND-DMT ratio from 1.34:1 to 1:1 increased the gel time from 14.1 to 32.75 min. and is no doubt due to the decrease in the amount of vanadium salt. However, after aging 1 to 2 weeks at 60°C, the two promoter solutions have about the same gel times. Although there is a fair amount of scatter in these results, there is no apparent change in reactivity at any of the three concentrations over the period of 93 days at 60°C, which is equivalent to about 3 years at ordinary temperatures. Addition of 0.55 phr of this promoter solution results in the same gel time as the addition of 0.28 phr of the Ten-Cem promoter solution. Times to maximum temperature and Barcol hardness remained essentially unchanged at each concentration also. Some precipitate was observed in this solution after a period of 7 days, and by the end of the study, the amount of precipitate had increased considerably.

TABLE 3. Aging of Promoter Solution<sup>a</sup> Made From 3% Vanadium Trineodecanoate.

Amount of promoter solution added (phr)	Age (days)	Gel time (min.)	Time to max. temp. (min.)	Barcol hardness
0.28	0	32.75	53.5	48
	7	34.25	57.75	49
	14	33.25	54.75	47
	21	33.75	55.75	50
	35	27.5	44.75	47
	54	28.75	47.5	49
	72	30.75	51	45
	93	31.75	52.25	48
0.37	0	15.5	24.25	47
	7	14.75	22.5	47
	14	20	31.5	48
	21	18.5	26.5	47
	35	19.5	30.5	46
	54	19.25	31	46
	72	15	23.25	47
	93	18.5	26.75	47
0.55	0	5.25	9.25	49
	7	8	13	48
	14	9	14	47
	21	10	16	49
	35	7.25	11.75	47
	54	7.75	12.5	49
	72	5.5	8.75	49
	93	5	10.25	47

<sup>a</sup> V salt solution to DMT ratio = 1:1; aged at 60°C.

The effect of vanadium trineodecanoate concentration in the promoter solution was also investigated. Since the initial concentration of the vanadium salt was 3%, xylene was either added or removed to give concentrations of 2 or 4%. Using a vanadium salt solution to DMT ratio of 1:1, the gel times were measured at three concentrations. The results are shown in Table 4 and Figure 1.

As expected, there is a wide spread of gel times observed ranging from 53.25 min. for the lowest amount of 2% VND to 2.5 min. for the largest amount of 4% VND. It can be noted here that on comparing gel times for the promoter using 3% VND solutions in Tables 3 and 4, the gel

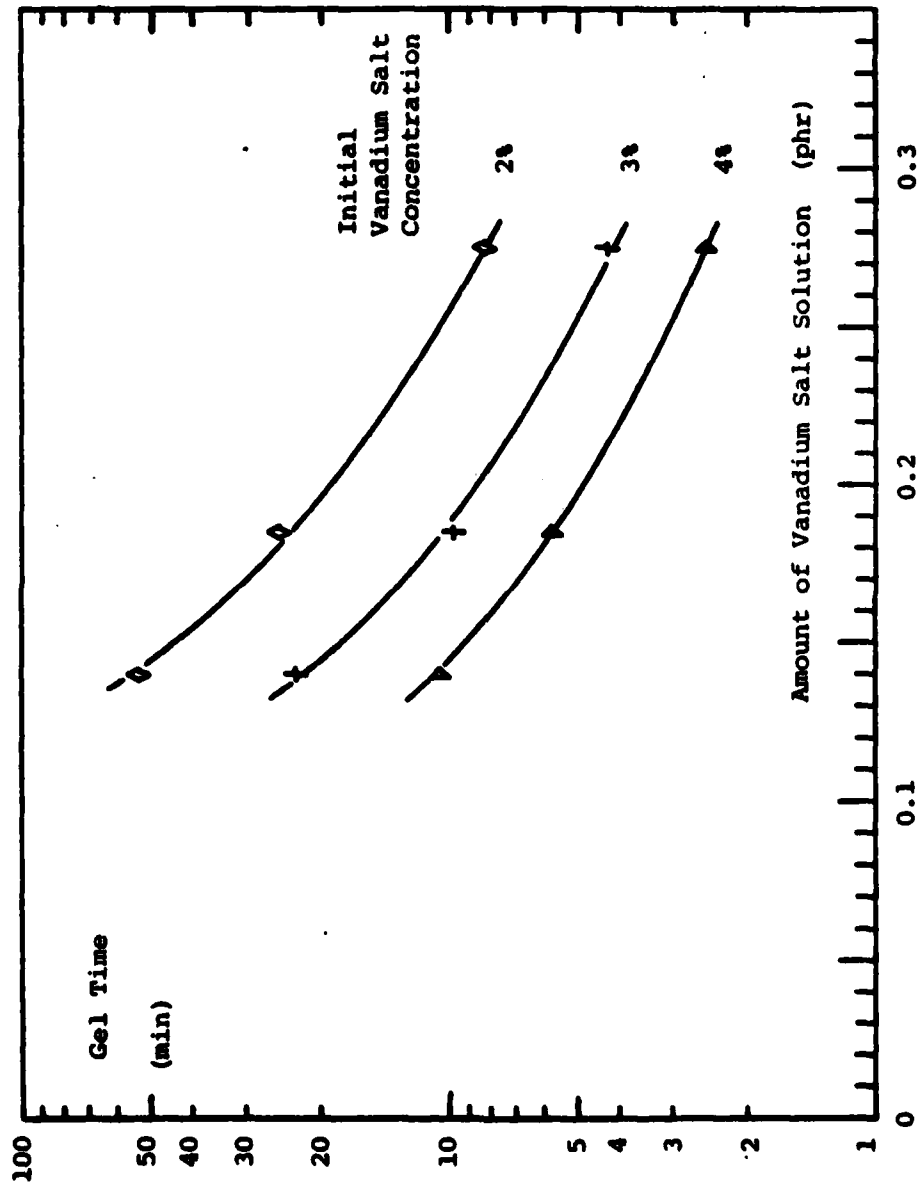


Figure 1: Effect of Vanadium Trineodecanoate Concentration on Gel Time

times are different. The only difference in procedure that could have caused this is that the promoter in Table 3 was premixed while for Table 4 the ingredients were added separately.

TABLE 4. Effect of VND Concentration on Reaction Times.

Initial VND conc. (%)	Amt. VND soln. added (phr)	Amt. DMT added (phr)	Gel time (min.)	Time to max. temp. (min.)	Barcol hardness
2	0.14	0.14	53.25	94.25	51
	0.185	0.185	25.0	40.0	47
	0.275	0.275	8.25	14.25	48
3	0.14	0.14	22.75	36.0	52
	0.185	0.185	9.75	15.5	52
	0.275	0.275	4.25	7.5	54
4	0.14	0.14	10.5	17.25	51
	0.185	0.185	5.75	10.0	55
	0.275	0.275	2.5	5.0	54

Because using a 4% vanadium salt concentration would mean having to transport less solution and the reactivity is similar to that of the Ten-Cem, a large-scale preparation of a 4% VND solution was carried out. No difficulties were encountered with the reactions using either pure or the less expensive technical grade ingredients. Table 5 presents a comparison of the results obtained with various 4% VND solutions. The VND and DMT were added separately in these tests. It is apparent that there is essentially no difference in the reactivity of these three solutions.

An accelerated aging study was then carried out at 60°C on a promoter solution prepared using a 1:1 ratio of 4% vanadium salt solution and DMT. Only the concentrations of 0.28 phr and 0.37 phr were investigated since the 0.55 phr concentration gave gel times too fast to be practical. It is obvious from the results in Table 6 that there is no aging effect with this solution either. The duration of the study, 79 days, is equivalent to about 2.5 years at ordinary temperatures. On comparing the results in Table 6 with those of Table 5, it can be seen that, in this case, adding the premixed promoter solution or the DMT and VND separately had no effect on the gel times.

Flexural strengths of laminates prepared with three different promoter solutions were measured and shown in Table 7. The desired goal<sup>2</sup> of 28,000 psi has been surpassed by every laminate shown except for the Ten-Cem laminate made under wet conditions. Low flexural strengths have been noted previously for laminates made in the presence of moisture.<sup>2</sup>

TABLE 5. Comparison of Various 4% Vanadium Trineodecanoate (VND) Solutions.

VND soln.	Amt. VND soln. added (phr)	Amt. DMT added (phr)	Gel time (min.)	Time to max. temp. (min.)	Barcol hardness
954-30 <sup>a</sup>	0.14	0.14	10.5	17.25	51
"	0.185	0.185	5.75	10.0	55
956-22 <sup>b</sup>	0.14	0.14	12.5	20.0	48
"	0.185	0.185	6.0	10.5	47
956-122 <sup>c</sup>	0.14	0.14	12.0	19.25	45
"	0.185	0.185	7.0	11.5	48

<sup>a</sup> Originally contained 3% VND; xylene evaporated off to give 4% VND; made with reagent grade V<sub>2</sub>O<sub>5</sub> and prime grade neodecanoic acid.

<sup>b</sup> Made with technical grade V<sub>2</sub>O<sub>5</sub> and prime grade neodecanoic acid.

<sup>c</sup> Made with technical grade V<sub>2</sub>O<sub>5</sub> and technical grade neodecanoic acid.

TABLE 6. Aging of Promoter Solution<sup>a</sup> Made From 4% Vanadium Trineodecanoate.

Amount of promoter added (phr)	Age (days)	Gel time (min.)	Time to max. temp. (min.)	Barcol hardness
0.28	0	12.25	19.25	47
	7	14.5	21.75	47
	21	12.25	18.5	49
	40	11.0	17.0	49
	58	12.0	18.75	46
	79	16.0	24.5	46
0.37	0	7.5	12.0	50
	7	7.5	11.75	49
	21	9.5	14.75	48
	40	7.0	11.5	47
	58	6.5	10.5	48
	79	7.75	12.25	49

<sup>a</sup> V salt solution to DMT ratio = 1:1; aged at 60°C.

TABLE 7. Flexural Strengths of Polyester-Glass Mat Laminates.

VND soln. used	Resin content (%)	Initial water content in glass mat, %	Avg. flexural strength <sup>a</sup>	
			GPa	psi
Ten-Cem <sup>b</sup>	55.6	0	0.271±.041	39300±5800
"	57.6	71.0	0.162±.019	23500±2800
3% <sup>b</sup>	55.6	0	0.368±.006	53400±900
"	55.9	67.8	0.243±.027	35300±4000
4% <sup>c</sup>	57.4	0	0.330±.036	47800±5200
"	54.4	70.7	0.192±.025	27800±3690

<sup>a</sup> Average obtained from 5 or 6 samples.

<sup>b</sup> Promoter solution had VND to DMT ratio of 1.34:1.

<sup>c</sup> Promoter solution had VND to DMT ratio of 1:1.

The greatest problems with obtaining good laminates under wet conditions are in getting good adhesion between the resin and the fiberglass and in avoiding bubbles of air or water entrapped within the fiberglass. The strengths exhibited by the laminates prepared with the new promoter solutions are significantly better than those made with Ten-Cem.

#### CONCLUSIONS

The following conclusions can be made in regards to this program:

1. A method for preparing vanadium trineodecanoate in xylene solution has been devised.
2. This vanadium salt solution at the 4% level is as reactive as Ten-Cem in the polyester-cumene hydroperoxide resin system.
3. The storage life of the vanadium salt solution is very good. The storage life of the VND-DMT promoter solution is also very good, especially if stored under nitrogen. Accelerated aging of the solutions for 175 days at 60°C, which is equivalent to about 5.5 years at 25°C, showed very little change in reactivity.
4. The formation of a precipitate which occurs with promoter solutions made with either Ten-Cem or our new vanadium salt solution on storage may cause clogging problems in the pumping/spraying system, but is not a problem as far as reactivity is concerned.

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5. Flexural strengths of laminates made with the new VND solutions under either dry or wet conditions meet or exceed specifications. They are significantly better than the strengths obtained for the laminates made by using Ten-Cem.

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## Appendix A

## PREPARATION OF VANADIUM TRINEODECANOATE SOLUTIONS

## 3% VANADIUM TRINEODECANOATE SOLUTION

To a stirred solution of 42 g of 90% formic acid in 450 ml of concentrated hydrochloric acid was added over 5 min. 54 g of powdered, reagent grade vanadium pentoxide (Note 1). The system was flushed with nitrogen, heated to 80°C and held at 80-90°C for 2 hours (Note 2). Without cooling, 330 g of neodecanoic acid (prime grade) (Note 3), 192 g of triethyl phosphate, 6 g of paraformaldehyde, and 500 ml of xylene were added. While maintaining a nitrogen atmosphere, the heterogeneous system was heated rapidly to reflux with very vigorous stirring (Note 4). The azeotroping aqueous phase was separated in the water trap and removed continuously; depending on the efficiency of the condenser, 410 to 440 ml of aqueous phase was recovered (Note 5). The pot temperature during this period was 100-110°C and only when most of the water had been removed did it rise slowly to 148-150°C. About 100 to 120 min. were required to complete the removal of the aqueous phase. When no more azeotrope distilled, the heating was stopped, the green-colored xylene solution was cooled (still under a nitrogen blanket) to 50°C and 5 g of Celite were added with stirring. The solution was vacuum-filtered through a Celite mat into a tared flask; the reaction vessel was washed with three 10-20 ml portions of xylene, each washing being used in turn to wash the Celite mat. The weight of the filtered solution was finally adjusted to 1,000 g with xylene (Note 6). The vanadium salt solution should probably be stored under nitrogen.

Notes:

1. A two-liter flask with stirrer, thermometer, nitrogen inlet, and a water separating trap fitted with a long, very efficient condenser, was used.
2. At this point the solution should have a deep green color and there should be no undissolved material.
3. The weight of neodecanoic acid is 5% more than theory assuming pure  $C_9H_{19}COOH$ . If other grades of neodecanoic acid are used, the weight

of acid actually employed should be adjusted for measured differences in equivalent weight or acid number.

4. It is essential to keep the two phases well dispersed and in intimate contact. An acid-stable emulsifying agent might be useful but was not tested.

5. The aqueous phase contains the excess hydrochloric acid and with fortification could probably be recycled in the next run. In the laboratory set-up some hydrogen chloride also escapes through the top of the condenser and could be trapped for reuse.

6. Theoretically, this solution should contain 3.0% vanadium; by analysis it was always slightly less, 2.8-2.9%.

#### 4% VANADIUM NEODECANOATE SOLUTION

The same procedure was used for preparing the 4% VND solution as was used for the 3%, except for the following:

a. The amount of xylene used for azeotroping the excess HCl was reduced to 250 ml; the quantities of other reactants were kept the same.

b. The final weight of the filtered solution was adjusted to 750 g instead of 1,000 g.

Technical grade vanadium pentoxide was used as a 1:1 replacement for reagent grade  $V_2O_5$ . The promoter made from this vanadium neodecanoate solution was as effective as that made from the reagent  $V_2O_5$ .

Both the reagent grade  $V_2O_5$  and the prime grade neodecanoic acid were replaced by technical grade reactants (the  $V_2O_5$  on an equal weight basis; 363 g of the technical grade acid was used instead of 330 g of the prime grade; the quantities of other reactants were the same as before except that only 250 ml of xylene were used). The promoter made from the resulting 4% vanadium solution was as effective in curing resin as those promoters made from the higher grade reactants.

Appendix B

ANALYSIS OF VANADIUM IN VANADIUM  
TRINEODECANOATE SOLUTION

The method of analysis, based on E. B. Sandell's colorimetric procedure for xylene-soluble solutions,<sup>3</sup> was as follows:

For a solution containing 1-4% vanadium, 1.00 ml of vanadium solution was extracted with several 10 ml portions of 2N HCl, and the combined aqueous extracts were diluted to 100 ml. A 2-ml aliquot of the diluted solution was oxidized to vanadium (V) by diluting to about 10 ml, adding about 50 mg potassium chlorate, and heating gently until the color of the solution changed to yellow. 10 ml of 1:2 H<sub>3</sub>PO<sub>4</sub> and 5 ml of 0.5 M sodium tungstate were added to the solution, and the final solution was diluted to 100 ml. The absorbance of the solution at 400 nm was determined. Vanadium concentration was obtained by comparison of the absorbance to absorbances of solutions of known vanadium concentration, prepared from chemically pure ammonium vanadate and treated in the same manner. The absorbances in the concentration range employed were a linear function of concentration, and for a 1-cm cell vanadium concentration was given by

$$\mu\text{g vanadium/ml} = \text{absorbance} \times 26.4.$$

## Appendix C

MEASUREMENT OF GEL TIME AND TIME TO  
MAXIMUM TEMPERATURE

The gel times of the polyester resin system were measured to the nearest 0.25 minute with a modified Tecam Gelation Timer [Techne (Cambridge) Ltd., Duxford, Cambridge, England]. The motor in the original timer which gave times only to the nearest minute (a 1-rpm motor) was replaced by a 4-rpm motor to give times to the nearest quarter minute. With this timer, a flat weighted disk, connected by a link with end play in it to a crank turned by the motor, falls under gravity in the polymer liquid, but is pulled up on the upstroke by the motor. At the gel point the rigidity of the polymer is sufficient to support the weight of the disk; this causes the link to be compressed which closes an electrical circuit and shuts off the motor. The original steel disk was replaced by disposable aluminum ones with steel washers added to make up the difference in weight.

Gel times were measured using 100 g samples of the polyester resin obtained from Port Hueneme (RS 50338) weighed out in 150 ml polypropylene disposable beakers. To this was added the desired quantity of promoter solution, or if the promoter solution was not premixed, the desired quantities of vanadium trineodecanoate solution and N,N-dimethyl-p-toluidine. The mixture was then stirred using a wooden tongue depressor (disposable) attached to a variable speed stirrer. 1.1 g of catalyst, cumene hydroperoxide, was then added and mixed into the polymer solution for 0.75 minute. The beaker was then placed under the gel timer so that the disk was located in the mixture about 1 cm from the bottom of the beaker at the lowest point of its downstroke. Exactly 1 minute elapsed between the start of mixing of the catalyst into the resin solution and the start of the gel timer. The temperature was monitored using a chromel-alumel thermocouple connected to a recorder; the thermocouple was inserted into a small disposable glass tube immersed in the resin solution. In this way, the time to maximum temperature was measured. The actual temperature reached was quite high, over 200°C in some instances, and the resulting polymer was highly fractured.

## Appendix D

## PERFORMANCE, PROPERTIES, STORAGE, AND HANDLING RECOMMENDATIONS

Use of the 4% VND solution with a VND to DMT ratio of 1:1 gives a promoter with a reactivity similar to that of the Ten-Cem. At 25°C with this promoter solution and with a cumene hydroperoxide concentration of 1.1 phr, average gel time properties should be:

Amt. promoter soln. added (phr)	Catalyst promoter ratio	Gel time (min.)	Time to max. temp. (min.)	Barcol hardness
0.28	4:1	12.5	20	45-50
0.37	3:1	7.0	12	45-50

The shelf life of the 4% VND has been shown to exceed 2.5 years at ordinary temperatures when mixed with DMT. The shelf life of the VND without the DMT should be even longer. From the aging data with the 3% VND, the shelf life of the 4% VND, by itself, should exceed the specified 5-year minimum. The mixed VND-DMT solution should probably not be stored longer than necessary because the precipitate that forms in time could clog the pumping system components.

No other catalyst concentrations or reaction temperatures were investigated in this program. However, any performance specification for this promoter solution should include such data and the performance at various humidities.

The flexural strength of laminates prepared with Fabmat C-4020 in the laboratory should well exceed the specified value of 0.193 GPa (28,000 psi). When made in the presence of moisture, the resulting laminate should at least meet the specified value.

The following properties are known:

- Specific gravity at 25°C: 3% VND-0.951 g/ml  
4% VND-0.993 g/ml

2. Color - dark green, clear liquid.

3. Odor - that of xylene.

Flammability - essentially that of xylene - dangerous when exposed to heat or flame; explosion hazard is moderate when vapors exposed to heat or flame. In case of fire, use NFPA Class B extinguishers (carbon dioxide, dry chemical or foam).

Toxicity - VND solution unknown. For components of the solution:

Xylene - an irritant to skin and respiratory system, vapors in high concentration are anesthetic; toxic if swallowed.

VND - unknown, but vanadium compounds are generally irritants to the conjunctivae and respiratory tract; may lead to pulmonary involvement.

Triethyl phosphate - unknown, but may cause nerve injury.

Storage and Handling - should be stored in glass bottles or glass-lined containers away from heat or flame. Xylene may attack some polyethylene or other types of plastic containers. Triethyl phosphate or any residual hydrochloric acid may attack metal containers.

In handling, measures should be taken to prevent eye contact, skin contact, or inhalation of vapors. Use only in well-ventilated areas away from all sources of heat, sparks, or flames. Contaminated clothing should be washed before reuse.

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