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**DUAL CURE LOW-VOC COATING PROCESS
Final Technical Report**

**By
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December 1993

Work Performed Under Contract No. AC04-88ID12692

**For
U.S. Department of Energy
Office of Industrial Technologies
Washington, D.C.**

**By
3M Company
St. Paul, Minnesota**

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**Prepared for the
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Under DOE Idaho Operations Office
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Office of Industrial Technologies
Washington, D.C.**

**Prepared by
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TABLE OF CONTENTS

Section	Page
INTRODUCTION	1
SUMMARY	1
TASK 1: DEVELOP DUAL CURE URETHANE/ACRYLATE	
AEROSPACE COATINGS	3
Sub-task 1.1: Select and Prepare Substrates	4
Sub-task 1.2: Optimize and Screen Coating Formulations	4
Sub-task 1.3: Qualification Test Selected Formulations	12
Sub-task 1.4: Determine and Optimize Application and Cure Techniques	14
TASK 2: DEVELOP DUAL CURE EPOXY/ACRYLATE	
AEROSPACE PRIMERS	20
Sub-task 2.1: Select and Prepare Substrates	21
Sub-task 2.2: Optimize and Screen Coating Formulations	21
TASK 3: DEVELOP SOLVENTLESS TAPE BACKING	29
Sub-task 3.1: Select Tape Backing Substrates	29
Sub-task 3.2: Determine Resin Formulation	30
Sub-task 3.3: Establish Curing Conditions	32
Sub-task 3.4: Prepare Pressure Sensitive Adhesive Tape	33
Sub-task 3.5: Evaluate Tape Properties	34
TASK 4: EVALUATE PROCESS PERFORMANCE	37
Sub-task 4.1: Evaluation of Technical Performance	37
Sub-task 4.2: Economic and Cost Analysis	48
Sub-task 4.3: Energy Analysis	55
TASK 5: REPORTS, CONTRACT ADMINISTRATION, AND TECHNOLOGY	
TRANSFER	69
Appendix 1: Comparison of Urethane Topcoat Requirements	71
Appendix 2: Comparison of Epoxy Primer Requirements	75

LIST OF TABLES

Table	Page
1.1: Performance testing results on "Flex 631" topcoat formulation	13
1.2: Performance testing results on "Flex 651" topcoat formulation	13
1.3: Performance testing results on BMS 10-60 control topcoat	14
3.1: Backing properties produced from dual cure epoxy saturant with different concentration of Flexibilizer 1	34
3.2: Performance properties of tapes produced from dual cure backings saturated with different concentration of Flexibilizer 1 and coated with either rubber based or acrylic based adhesive	35
3.3: Physical performance properties of tapes produced from dual cure backings and rubber based adhesive along with control tape samples.....	35
3.4: Electrical performance properties of tapes produced from dual cure backings and rubber based adhesive along with control tape samples.....	36
4.1: U.S. Energy savings resulting from solvent elimination by market area (million pounds, trillion Btu/year)	60
4.2: Energy required for curing various coating types	61
4.3: Energy savings for dual cure replacing other curing methods.....	63
4.4: Projected volumes by cure type in 2010 and corresponding savings by use of dual cure	64

FINAL TECHNICAL REPORT
DoE CONTRACT DE-AC04-88ID12692
DUAL CURE LOW-VOC COATING PROCESS
PHASE III

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is implementing increasingly stringent environmental regulations designed to minimize or eliminate the emissions of volatile organic compounds (VOCs). VOC emissions total about 7×10^9 lbs/yr, a large portion of which is due to paints and other coating systems used by industry. At a minimum, the cost of disposing of these hydrocarbon wastes is increasing and, as a further disincentive, the manufacturer retains long-term liability for wastes after disposal. Low-cost, monomer formulations, containing little or no VOCs, are needed to reduce emissions and to save the energy currently put into the manufacture and disposal of the VOCs and into the curing of the coatings.

SUMMARY

This is the final technical report for the cost-shared project with DoE. It describes Phase III, proof-of-principle testing, in detail, and includes, by reference, Phase I and Phase II.

The objective of 3M's contract with the U.S. Department of Energy DE-AC04-88ID12692 is to develop Dual Cure Photocatalyst coating technology to save energy and reduce gaseous waste emissions through the minimization of coating solvent use. This is to be accomplished by developing a photocuring technology that would allow the use of solvent free (100% solids) or reduced solvent content formulations while preserving or improving upon the performance of conventional solvent based materials.

Phase III of the project focused on proof-of-principle testing in full-scale systems of the dual cure photocatalyst technology developed in earlier phases of the program. The Phase III commercial applications identified for demonstrating the utility of the dual cure photocatalyst technology are aerospace topcoats, aerospace primers, and solventless manufacture of tape backings. Aerospace topcoat formulations, based on urethane/acrylate systems, were developed which meet essentially all of

the initial screening test criteria. Optimization of the formulation was carried out through the use of statistical formulation design experiments. A large scale application and cure demonstration was conducted at Boeing.

Technical challenges were encountered with the epoxy/acrylate aerospace primer formulation. As a result of cure consistency problems resulting from moisture inhibition along with the increased need for non-chromated primers, work on the aerospace primer system was de-emphasized to allow for greater effort on the development and commercialization of the aerospace topcoat.

Work on the third demonstration application, development of solventless saturants for electrical tape backings, was successfully completed. Optimal 100% solids dual cure resin formulations were identified and utilized in preparing complete tape constructions. These tapes were evaluated and characterized in terms of benchmark U.L. and internal 3M specifications for electrical tape performance. In most cases the properties of the tapes produced from the dual cure backings were comparable to the control products currently being made by solvent based processes. Both pilot scale and factory scale coating trials were completed using the dual cure formulations.

Cost, economic, and energy analyses conducted during Phases I and II were updated based on the information obtained in Phase III. Substantial reductions in volatile organic compounds emissions in the U.S. are estimated from the projected use of dual cure photocatalyst technology. Based on the successful demonstration of production scale processing and the potential economic, environmental and energy benefits, full commercial implementation of the dual cure tape backing saturant is currently under consideration at 3M. Further development and commercialization of the aerospace topcoat is being reviewed based on the results of further assessments being conducted by Boeing on the feasibility of implementing a photocurable paint system in their manufacturing operation.

Branching off from this project, 3M, on its own funding, has already commercialized the dual cure technology in its line of flexible diamond resin products. Formulated as a binder, the dual cure material exhibits superior properties in holding the finer-grit diamond particles and produces better cut and finish, along with improved life when used in polishing granite tile surfaces, than previously possible with solvent-based binders.

TASK 1: DEVELOP DUAL CURE URETHANE/ACRYLATE AEROSPACE COATINGS

The goal of this task was to develop a dual cure urethane/acrylate aerospace coating which meets the performance requirements of existing solvent borne urethane topcoats. Current materials are qualified under one of three specifications: MIL-C-83286 "Aliphatic Isocyanate Urethane Coating for Aerospace Applications" for low solids solvent based urethanes, MIL-C-85285 "High Solids Polyurethanes", or Boeing Material Specification (BMS) 10-60 "Protective Enamel" for commercial aircraft topcoats. The key requirements for each of these specifications are summarized in Appendix 1.

Four sub-tasks were performed for the urethane/acrylate coating task:

Sub-task 1.1– Select and prepare suitable substrates for testing.

Sub-task 1.2 – Optimize and screen coating formulations using a series of tests selected from the qualification standards.

Sub-task 1.3 – Perform testing at 3M and Boeing Defense and Space Group of selected formulations using a wider range of the qualification tests.

Sub-task 1.4 – Determine and optimize application and cure techniques for the dual cure urethane/acrylate compositions.

There was considerable overlap between the individual tasks, especially sub-tasks 1.2 and 1.3 which involved screening and optimization of topcoat formulations and qualification testing of these formulations.

At the end of the first six months of the Phase III contract, substrate preparation had been completed, a formulation had been developed which largely met the screening requirements, and the second stage of qualification testing, including accelerated weathering, had been started. The efforts in the second six months of the Phase III contract focused on improving gloss and accelerated weathering performance of the coating while maintaining the performance level of the other screening criteria. As a result of poor weathering performance, the urethane/acrylate topcoat formulation had to be significantly modified. During the third six month period, formulations were developed which met essentially all of the initial screening test criteria including accelerated weathering performance. Optimization of the formulation was carried out through the use of statistical formulation design experiments. During the fourth six

month period, further optimization of the formulation was conducted along with determination and optimization of application and cure techniques for the dual cure urethane/acrylate compositions. A large scale application and cure demonstration was successfully conducted at Boeing.

Sub-task 1.1: Select and Prepare Substrates

Three types of test panels were obtained and used: bare aluminum without surface-treatment (Q-panels); alodine treated 2024 aluminum panels (chromate anodized); and primed aluminum panels prepared by Boeing. Primed aluminum panels obtained from Boeing were prepared using either a waterborne epoxy primer (MIL-P-85582 or BMS 10-11) over 2024 T3 aluminum or a solvent borne epoxy primer (BMS 10-79) over 2024 T3 aluminum. The various topcoat specification documents provide explicit guidance for surface preparation of panels for each of the tests.

Sub-task 1.2: Optimize and Screen Coating Formulations

A series of screening tests were identified for performing initial evaluation of topcoats relative to the military and commercial specifications. These tests were selected to allow rapid assessment of coating performance and evaluation of the impact of formulation changes. The screening tests proposed were: pencil hardness; 60 degree gloss, impact flexibility, wet tape adhesion, cold temperature bending, 7 day Skydrol resistance, distilled water resistance, and salt spray resistance.

After the start of Phase III, it was determined that wet tape adhesion and distilled water resistance did not present a problem for any of the formulations initially examined. Lack of ready access to a -65°F chamber made the cold temperature bending test too difficult to perform on a routine basis if it were used as a screening criteria. Therefore, it was decided to include this test in the qualification testing performed at Boeing. The 500 hour (almost 21 days) requirement for salt spray resistance made this test less useful for screening formulation changes due to the time required to complete the test. In practice, little problem was encountered in meeting the salt spray requirement for any formulations tested. Therefore, the focus of the sub-task 1.2 screening activity was on pencil hardness, 60 degree gloss, impact flexibility, and 7 and 30 day resistance to Skydrol hydraulic fluid. Once initial baseline formulations were identified, it was determined that it was necessary to include 500 hour Xenon accelerated weathering in the screening tests. In

addition to these tests, VOC levels were routinely measured to assure that adequate cure was being achieved.

As the result of previous work, a baseline formulation was identified at the beginning of Phase III and is shown below.

35%	Pigment (TiO ₂)
65%	Resin, consisting of
	70% Urethane Precursors
	1:2 ratio of Polyol 1 & Polyol 2
	Isocyanate 1
	30% Acrylates
	70% Diacrylate 1
	30% Monoacrylate 1
0.1%	Iron photocatalyst (CpFeXylPF ₆) (on total resin wt.)
0.7%	Dispersant 1 (2% on pigment)
0.4%	Co-catalyst 1 (2% of acrylate resin)

Iron photocatalyst levels are always expressed as a percentage of the total resin weight, while co-catalyst levels are normally expressed as a percentage of the acrylate weight, and dispersants are normally expressed as a percentage of the pigment weight.

Initial evaluations indicated that three significant issues needed to be addressed with this formulation. These included: (1) a need to improve the degree of acrylate cure, (2) a need to improve the reverse impact performance of the coating, and (3) a need to improve the gloss of the coating.

Through the use of VOC level tests, it was determined that approximately 50% of the acrylate resin was remaining uncured after 15 minutes of exposure to Super Diazo Blue lights at room temperature. The acrylate portion of the formulation cures via a free radical mechanism. Both the radicals resulting from decomposition of the photocatalyst and radicals from the iron catalyzed decomposition of the co-catalyst act to cure the acrylate. The primary inhibitor to the acrylate cure was presumed to be oxygen diffusion into the wet coating. Several approaches were considered to improve the acrylate cure: increasing the photocatalyst concentration, changes in the co-catalyst concentration and type, addition of oxygen scavengers, and addition of other additives, such as surface blocking agents.

The most significant effects on acrylate cure were found to be the co-catalyst concentration and iron photocatalyst concentration. The concentration of co-catalyst 1 was found to have a significant effect up to the 1% level (based on the acrylate resin), but no additional benefits were found for higher co-catalyst levels. The concentration of iron photocatalyst was found to increase the acrylate cure at higher concentrations. Based on these results, the standard catalyst system used for the urethane/acrylate topcoats was changed from 0.1% to 0.25% iron photocatalyst (CpFeXylPF_6) and the co-catalyst level was maintained at the 2% level. The addition of oxygen scavengers was also found to improve acrylate cure in the formulations evaluated. Using the 0.25% iron photocatalyst level with 2% Co-catalyst 1, it was concluded that 5% of oxygen scavenger 2 yielded the best results.

Taken in combination, the steps of increasing iron photocatalyst concentration and adding an oxygen scavenger were sufficient to raise the level of acrylate conversion from approximately 50% to the low 90% range. When the functional performance of the resin formulation was tested, it was found that the coating was too brittle to provide the required impact flexibility. Test panels, which showed good VOC performance, failed reverse impact at 10 to 20 in-lbs. To address this problem, reformulation of the mixture to reduce the crosslink density in both the urethane and acrylate components was attempted. This was accomplished by modifying the polyol portion of the urethane, modifying the monoacrylate or diacrylate selected, and changing the monoacrylate to diacrylate ratio. Modifications in the urethane portion from a mixture of Polyol 1 and Polyol 2 to pure Polyol 2 and a change in the ratio of monoacrylate to diacrylate from 30/70 to 70/30, yielded a formulation which was very close to meeting the initial screening requirements, except for poor gloss.

Several experimental approaches were considered to improve the gloss, including formulation changes to improve the compatibility of the urethane and acrylate phases, reduction in the pigment loading, improvement in the milling procedure, and the addition of additives to improve the flow, leveling, or dispersion of the coating. A change in the milling method from a Cowles blade to a 3 roll mill produced an average improvement of 7 units in gloss. The pigment loading was found to strongly affect the gloss. Reductions in pigment loading were also found to provide slight improvements in the reverse impact performance. The VOC levels, when computed on the resin present basis, showed no effect of pigment loading on VOC.

Since formulations had been developed which were very close to meeting the screening requirements, selected formulations were chosen for accelerated weathering. All the formulations selected for initial weathering were based on the same bulk ratio of urethane to acrylate, pigment loading, and identical urethane resins and catalyst systems. The only variation was in the acrylate portion of the resin. Two monoacrylates, Monoacrylate 1 and 2, and two diacrylates, Diacrylate 1 and 4, were selected. The four possible monofunctional and difunctional acrylate combinations were prepared, knife coated on panels, and submitted for 500 hour salt spray and Xenon accelerated weathering tests. At this stage in the formulation development, the baseline urethane/acrylate topcoat formulation consisted of the composition shown below.

35%	Pigment (TiO ₂)
65%	Resin, consisting of
	70% Urethane Precursors
	Polyol 2
	Isocyanate 1
	30% Acrylates
	70% Monoacrylate 1 or Monoacrylate 2
	30% Diacrylate 1 or Diacrylate 4
0.25%	Iron photocatalyst (CpFeXylPF ₆) (on total resin wt.)
0.7%	Dispersant 1 (2% on pigment)
0.4%	Co-catalyst 1 (2% of acrylate resin)
1.0%	Oxygen Scavenger 2 (5% of acrylate resin)

All four acrylate combinations in the baseline formulation passed the 500 hour salt spray requirement. However, at 500 hours of accelerated weathering in the Xenon weatherometer, all samples showed a significant decrease in gloss to levels below 10%. This type of behavior was not observed with clearcoat urethane/acrylate formulations subject to Xenon weatherometer during Phase II. Due to the poor results of the initial formulations described in Table 1.1, efforts were focused on identifying means of improving the accelerated weathering performance of these pigmented urethane/acrylate coatings.

Several U.V. absorber/light stabilizer combinations were evaluated in these baseline formulations. The presence of the U.V. absorber/light stabilizer was found to have two main effects. First, they reduced the initial gloss of the samples. Secondly, these additives appeared to delay the rapid drop in gloss with accelerated weathering. However, the gloss

after 500 hours was only slightly higher than those samples without these stabilizers.

In an attempt to isolate the cause of the poor weathering performance, the following pigmented samples were prepared: pure urethane (based on Polyol 2 And Isocyanate 1); urethane plus Co-catalyst 1; urethane plus Co-catalyst 1 and Oxygen Scavenger 2; and the four urethane/acrylate combinations without Oxygen Scavenger 2. Initial gloss was measured and the samples were subjected to 245 hours in the Xenon weatherometer chamber. The gloss of all of the samples decreased rapidly in accelerated weathering. Based on these results, Polyol 2 was determined to be the primary cause of the poor weathering behavior. Work began on trying to identify a replacement for Polyol 2 which would result in improved weathering while maintaining the other performance properties. Based on a series of test results on pure urethane formulations and complete pigmented urethane/acrylate compositions, a 70/30 blend of Polyol 1 and Polyol 3 was identified as a candidate for further evaluations.

A series of auxiliary compounds to accelerate the catalyst activity were examined in an attempt to improve the surface cure of the urethane/acrylate formulations and hence improve the gloss. These accelerates were found to result in significantly improved initial gloss values. However, in most cases addition of an accelerant caused some discoloration. The accelerants appeared to have negligible effect on VOC emissions. Accelerant 10 was identified as the most promising candidate for further evaluation since it seemed to represent the best compromise between initial gloss and discoloration.

Samples containing different types and concentrations of light stabilizers and U.V. absorbers were prepared and evaluated. All of the samples with a U.V. light absorber/light stabilizer combination had less gloss reduction during Xenon accelerated weathering than the control samples. From these results it was concluded that the optimum light stabilizer is #4 at a concentration of approximately 1.5% with no strong dependence observed for U.V. absorber type or concentration in this formulation.

Due to the complexity of the formulation and the apparent interdependence of several of the components on the various performance properties, a designed experiment was determined to be in order. With the assistance of 3M internal statistical consulting staff, a mixture design experiment was laid out to evaluate the effect of five of the primary formulation components on coating performance properties. The variables that were evaluated included: Polyol 1 level; Polyol 3 level; Monoacrylate 2 level;

Diacrylate 4 level; and Light Stabilizer 4 level. The design called for the preparation of 35 formulations, which were prepared, knife coated, and cured. All of the samples were evaluated for VOC level, pencil hardness, gloss, reverse impact, 7 and 30 day Skydrol resistance, and Xenon accelerated weathering.

Complete test results from the five component mixture design experiment were obtained and analyzed. None of the individual design points met all of the screening performance factors. Gloss retention during 500 hour Xenon accelerated weathering was determined to be the most limiting performance factor. Reverse impact greater than 60 in-lbs, initial gloss greater than 90, and 7 day Skydrol resistance with a decrease in pencil hardness of less than or equal to one pencil hardness unit was also determined to be significant limiting performance factors. The resulting computer model predicted that a formulation does exist within the design space evaluated which meets all of the screening criteria. The predicted optimum formulation to meet all of the screening criteria is shown below.

35%	Pigment (TiO ₂)
65%	Resin, consisting of
	75% Urethane Precursors
	85:15 ratio of Polyol 1 to Polyol 3
	Isocyanate 1
	25% Acrylates
	70% Monoacrylate 2
	30% Diacrylate 4
0.25%	Iron photocatalyst (CpFeXylPF ₆) (on total resin wt.)
0.7%	Dispersant 1 (2% on pigment)
0.4%	Co-catalyst 1 (2% of acrylate resin)
1.0%	Oxygen Scavenger 2 (5% of acrylate resin)
2.0%	Light Stabilizer 4
1.0%	Accelerant 10

This represented a change in the polyol blend from 70:30 to 85:15 and a decrease in the acrylates from 30% of the resin to 25% of the resin. The predicted optimum formulation was prepared, knife coated, cured, and then tested for all of the screening criteria. This formulation met all of the screening specifications with the exception of initial gloss and 500 hour accelerated weathering. The gloss value decreased to 64% after 500 hours in the weatherometer from an initial value of 89%. The other performance properties were very similar to those predicted by the computer model, with the exception of reverse impact which was measured to be 40 in-lbs as compared to a predicted value of 60 in-lbs.

An alternate polyol was identified as a potential replacement for Polyol 1. This polyol (Polyol 6) is available in higher solids from the manufacturer and has lower viscosity. Substituting this polyol in the optimum formulation from the designed experiment resulted in approximately a 25% reduction in viscosity. The incorporation of Polyol 6 was found to result in lower VOC levels, increased reverse impact, along with comparable hardness, and initial gloss, but lower Skydrol resistance and accelerated weathering performance.

Moisture analysis of the mill base used to prepare the optimum formulation from the five component mixture design indicated a 0.5% water content. A commercially available moisture scavenger was identified and evaluated in the formulation at 9 and 18 parts per part of water. Mill bases were prepared with the moisture scavenger and the formulations were knife coated, cured, and evaluated for reverse impact, pencil hardness, Skydrol resistance, initial gloss, and Xenon accelerated weathering. The addition of the moisture scavenger appeared to increase the initial gloss and weathering performance without a sacrifice in the other properties.

Samples of pure urethane (based on Polyol 1 and 3 with Isocyanate 1) with TiO_2 pigment were prepared and submitted for accelerated weathering to determine if residues from the iron photocatalyst were interfering with the light stabilizer additives and resulting in decreased weathering performance. The samples that were evaluated included the following curatives: the iron photocatalyst alone; the iron photocatalyst in combination with Co-catalyst 1; and dibutyltin dilaurate (a commonly used, commercially available urethane thermal catalyst). All three samples had similar initial gloss values of approximately 93%. After 500 hours of accelerated weathering the tin catalyzed sample had decreased in gloss by 2%, while the iron photocatalyst alone and iron photocatalyst with co-catalyst decreased by 6 and 13%, respectively. The dibutyltin dilaurate catalyzed samples had a gloss value of 84% after 1000 hours of Xenon accelerated weathering. The samples which contained the iron photocatalyst alone and the iron photocatalyst in combination with the co-catalyst had gloss values of approximately 20% and 10%, respectively. These results indicate that the presence of iron photocatalyst has a significant detrimental effect on the accelerated weathering of pigmented urethane materials. Scanning electron photomicrographs of weathered samples reveal that gloss reduction during weathering is the result of resin erosion and pigment exposure at the coating surface. Reflective infrared spectra show no obvious changes in the chemical composition of

the weathered surface that would indicate the nature of the chemistry that might be occurring at the exposed surface.

A designed experiment was conducted on the following four variables in the optimized urethane/acrylate topcoat formulation: Oxygen Scavenger 2 level; photocatalyst level; Co-catalyst 1 level; and surface cure Accelerant 10 level. The results indicate that the levels of photocatalyst, co-catalyst, and surface cure accelerant should be decreased, while the level of oxygen scavenger should be increased to obtain optimal performance. Samples prepared with these formulation changes were found to result in improved accelerated weathering performance as compared to control samples.

A number of dispersants were screened in order to find one which would work with the lower viscosity alternative, hard polyol (Polyol 6). An optimized dispersant was identified and full formulations prepared using this dispersant. Test results indicate that the formulation containing the optimized dispersant had improved initial gloss, higher reverse impact and acceptable 7 day Skydrol resistance as compared to formulation containing the old dispersant. Accelerated weathering results of sprayed samples, prepared from formulations containing this polyol, were found to have gloss values of approximately 82% after 500 hours and greater than the specification value of 70% after 600 hours. However, rapid decrease in gloss was observed for exposure times greater than 600 hours. This more flexible formulation still appears to be marginal in terms of 30 day Skydrol resistance, with measured pencil hardness of 3B and the specification calling for 2B.

A series of samples with different Polyol 1 to 3 ratios in the optimized polyol ratio had a significant effect on reverse impact and only a minor effect on initial pencil hardness, initial gloss and 7 day Skydrol resistance. Thirty day Skydrol resistance and 500 hour accelerated weathering results indicated that a Polyol 1/3 ratio of 70:30 or greater is required to pass the 30 day Skydrol test. Dropping the polyol ratio from the current level of 85:15 to 40:60 had only a minor negative effect on accelerated weathering performance.

At this stage in the formulation development, two urethane/acrylate topcoat formulations had been identified as candidates for further testing. These formulations consisted of the compositions shown below.

"Flex 651" formulation:

35% Pigment (TiO₂)
65% Resin, consisting of
75% Urethane Precursors
70:30 ratio of Polyol 1 to Polyol 3
Isocyanate 1
25% Acrylates
70% Monoacrylate 2
30% Diacrylate 4
0.25% Iron photocatalyst (CpFeXylPF₆) (on total resin wt.)
0.7% Dispersant 1 (2% on pigment)
0.4% Co-catalyst 1 (2% of acrylate resin)
1.0% Oxygen Scavenger 2 (5% of acrylate resin)
2.0% Light Stabilizer 4
1.0% Accelerant 10
Flow control and leveling additives

"Flex 631" formulation:

35% Pigment (TiO₂)
65% Resin, consisting of
75% Urethane Precursors
70:30 ratio of Polyol 6 to Polyol 3
Isocyanate 1
25% Acrylates
70% Monoacrylate 2
30% Diacrylate 4
0.25% Iron photocatalyst (CpFeXylPF₆) (on total resin wt.)
0.7% Dispersant 10 (2% on pigment)
0.4% Co-catalyst 1 (2% of acrylate resin)
1.0% Oxygen Scavenger 2 (5% of acrylate resin)
2.0% Light Stabilizer 4
1.0% Accelerant 10
Flow control and leveling additives

Sub-task 1.3: Qualification Test Selected Formulations

Due to the overlap between sub-tasks 1.2 and 1.3 and the need to perform the work simultaneously, the majority of the results from both sub-tasks are reported above under sub-task 1.2. However, several formulations were submitted to Boeing Defense and Space Group to verify test results and to perform additional qualification testing. Some discrepancies were

identified in the results generated at 3M and at Boeing. 3M sprayed and cured the two formulations, identified as "631 flex" and "651 flex" above, on test panels primed by Boeing with BMS 10-11 and BMS 10-79 primers. Boeing sprayed and cured the two formulations, along with a BMS 10-60 Type II control, on test panels primed with MIL-P-85582. Sprayed and cured panels were exchanged to allow cross-checking the test results between the two laboratories. The results from these tests are summarized in the Tables 1.1 through 1.3 below.

Table 1.1: Performance testing results on "Flex 631" topcoat formulation.

Sprayed at:	3M		Boeing	
Tested at:	3M	Boeing	3M	Boeing
Gloss on BMS 10-11	84.4	87.1		
Gloss on BMS 10-79	89.6	87.2		
Gloss on MIL-P-85582			92.7	91.4
Initial Pencil Hardness	HB	HB	*	2B
7 day Skydrol	5B	B	*	2B
30 day Skydrol	5B	F	*	HB
Reverse Impact [in-lb]	90	72	88	60
Gloss after 500 hr QUV	77	57	73	
Gloss after 500 hr Xenon	79		73	

Table 1.2: Performance testing results on "Flex 651" topcoat formulation.

Sprayed at:	3M		Boeing	
Tested at:	3M	Boeing	3M	Boeing
Gloss on BMS 10-11	82.6	83.7		
Gloss on BMS 10-79	75.5	81.6		
Gloss on MIL-P-85582			89.5	84.4
Initial Pencil Hardness	HB-F	B	*	2B
7 day Skydrol	3B	F	*	2B
30 day Skydrol	3B	F	*	HB
Reverse Impact [in-lb]	103	75	80	56
Gloss after 500 hr QUV	67	49	70	
Gloss after 500 hr Xenon	71		67	

Table 1.3: Performance testing results on BMS 10-60 control topcoat.

Sprayed at:	3M		Boeing	
Tested at:	3M	Boeing	3M	Boeing
Gloss on BMS 10-11				
Gloss on BMS 10-79				
Gloss on MIL-P-85582			93.3	
Initial Pencil Hardness			*	
7 day Skydrol			*	
30 day Skydrol			*	
Reverse Impact [in-lb]			77	
Gloss after 500 hr QUV			76	
Gloss after 500 hr Xenon			88	

* All panels sprayed at Boeing, including the BMS 10-60 control, and tested at 3M failed the Skydrol resistance test after 7 days immersion. By 30 days all of the coatings had blistered and bubbled off of the panels, failing at the primer/panel interface. Based on these results, the preparation of the primed panels used in these tests is suspected to be out of specification.

A large panel application and cure demonstration were conducted at Boeing in Seattle, Washington on August 19, 1993. The demonstration included spraying and curing a window belt panel (~3'x5') primed with BMS 10-79. Test panels sprayed the day before indicated that dry to tape time as low as 1 hour after spraying was achievable. The demonstration was attended by representatives from: 3M Corporate Research; 3M Aerospace Materials Department; Department of Energy; Boeing Space and Defense Group; Boeing Materials and Testing (Commercial); and Boeing Manufacturing. The demonstration was followed by a 3M presentation and discussions on the dual cure technology and its applicability to aerospace topcoats. One of the major advantages of the dual cure technology was the ability to "cure on demand" and potentially reduce the cycle time required to paint an aircraft.

Sub-Task 1.4: Determine and Optimize Application and Cure Techniques

The majority of the formulation experiments described under sub-tasks 1.2 and 1.3 was performed using knife coated test panels. Most formulation experiments were performed using the same cure conditions: 15 minute solvent flash period followed by 15 minute exposure under Super Actinic Bulbs at a lamp distance of approximately 4 inches and at ambient temperature.

It was determined that the addition of some solvent was required to achieve sprayable viscosities. Initial spraying trials were conducted using a topcoat formulation containing 35% pigment, Polyol 1 and 3, and a 70/30 urethane to acrylate ratio with two different solvent mixtures. Several problems were encountered when these formulations were sprayed using conventional air spraying equipment. The formulations were found to have poor leveling characteristics, excessive sagging when sprayed on vertical surfaces, and pin-hole surface defects resulting from solvent popping. Anti-sag additives were found to be effective in reducing sagging and running of the topcoat; however, a detrimental effect on leveling of the sprayed coating was observed.

A high-volume low-pressure (HVLP) spray gun was acquired for spray trials. This is the only type of spray gun, with the exception of electrostatics, which is currently allowed by the South Coast Air Quality Management District Rulings for aerospace coatings. A number of trials were conducted using this spray gun. A number of different thinning solvents and solvent mixtures were evaluated. A 60/40 blend of PM acetate/methyl ethyl ketone appeared to provide the best spray performance.

The formulation viscosity as a function of temperature was measured for both an unthinned formulation and a formulation that had been thinned with approximately 10% PM acetate. A strong temperature dependence of the formulation viscosity was noted, as a 4 fold decrease in viscosity was observed when the formulation temperature was increased only 25°C (from room temperature to approximately 45°C). A viscosity of 300 cP was achieved on the formulation thinned with 10% solvent at 45°C. Without heat approximately 16% solvent is required to achieve a comparable viscosity. This lower solvent level corresponds to approximately 80 to 100 g/l lower VOC level.

Comparisons between spray applied and knife coated samples with the same formulations indicated that some differences in the coating performance based on the coating technique utilized were apparent. In general, spray applied formulations had higher pencil hardness, and improved gloss retention during accelerated weathering. The down side appeared to be a decrease in reverse impact performance in the spray applied samples. The optimum formulation when spray applied was found to have a reverse impact of 25 in-lbs, pencil hardness of 4H and a gloss level of 73% after 500 hours of accelerated weathering as compared to 40 in-lbs, 2H pencil and 64% gloss for the same formulation when knife

coated. It was speculated that the difference in performance between spray applied and knife coated samples is the result of some acrylate resin loss during spraying. Non-pigmented clearcoat formulations were prepared and both spray applied and knife coated. Analytical techniques were utilized to determine that measurable differences in urethane to acrylate ratio can be detected between the two different application techniques.

The relationship between lamp intensity, temperature, and cure time was determined. Set-to-cotton and dry-to-tape times for the "Flex 631" formulation was determined with two different light set-ups and different temperatures. These results are summarized below.

The first set-up involved determining "set-to-cotton" and "dry-to-tape" times of the dual cure topcoat at different temperatures with a Philips Super Actinic Fluorescent lamp set-up.

Set-up: six 18" 15 watt (Philips TLD15W/03) fluorescent bulbs at a distance of 4 inches from the test panels. Test panels were placed on a thermostated platen to maintain temperature.

Measured average intensity (over full spectral range): 3.56 milliwatts/cm².

Set-to-cotton time:

Experimental procedure: Panels were knife coated with the Dual Cure formulation at a thickness of 3 mils and allowed to stand at room temperature for 15 minutes to allow for solvent flash. The panels were placed on the thermostated platen and exposed to the Super Actinic lights for up to 15 minutes while testing to determine if the coating was set-to-cotton. Set-to-cotton time was determined when no fibers from a cotton ball adhered to the coating. If the panels were not set-to-cotton after 15 minute light exposure, then the panels were placed in the dark and examined periodically to determine set-to-cotton time.

Results:

Platen Temperature	Set-to-Cotton
20°C (68°F)	3 hours

30°C (86°F)	12 minutes
40°C (104°F)	4.5 minutes
50°C (122°F)	1.75 minutes

Dry-to-Tape time:

Experimental procedure: Panels were knife coated with the Dual Cure formulation at a thickness of 3 mils and allowed to stand at room temperature for 15 minutes to allow for solvent flash. The panels were placed on the thermostated platen and exposed to the Super Actinic lights for various lengths of time. Strips of 3M Scotch™ #250 tape were placed on the panels immediately after removal from under the lights and for every 30 minutes thereafter for up to 3.5 hours. Dry-to-tape time (a.k.a. "resistance to marring by tape") was determined using the procedure spelled out in BMS 10-60 section 8.2.7.

Results:

Platen Temperature	Exposure Time	Dry-to-Tape Time
30°C (86°F)	12 minutes	> 3.5 hours
30°C (86°F)	15 minutes	> 3.5 hours
50°C (122°F)	2 minutes	> 3.5 hours
50°C (122°F)	4 minutes	> 3.5 hours
50°C (122°F)	8 minutes	3.0 hours
50°C (122°F)	15 minutes	immediately out from lights

Minimum dose required for rapid (< 1 hour) dry-to-tape:

$$\begin{aligned}
 \text{Dose} &= \text{Intensity} \times \text{Time} \\
 &= 3.56 \text{ mw/cm}^2 \times 900 \text{ sec} \\
 &\sim 3.2 \text{ J/cm}^2
 \end{aligned}$$

The second set-up involved determining "set-to-cotton" and "dry-to-tape" times of the dual cure topcoat at different temperatures with a Sylvania Super Diazo Blue Fluorescent lamp set-up.

Set-up: four 60" (Sylvania F59.83"T12/SDB/VHO/LT) fluorescent bulbs at a distance of 4 inches from the test panels. Test panels were placed on a thermostated platen to maintain temperature.

Measured average intensity (over full spectral range): 4.99 milliwatts/cm²

Set-to-cotton time:

Experimental procedure: Panels were knife coated with the Dual Cure formulation at a thickness of 3 mils and allowed to stand at room temperature for 15 minutes to allow for solvent flash. The panels were placed on the thermostated platen and exposed to the Super Diazo Blue lights for up to 15 minutes while testing to determine if the coating was set-to-cotton. Set-to-cotton time was determined when no fibers from a cotton ball adhered to the coating. If the panels were not set-to-cotton after 15 minute light exposure, then the panels were placed in the dark and examined periodically to determine set-to-cotton time.

Results:

Platen Temperature	Set-to-Cotton
20°C (68°F)	1.75 hours
30°C (86°F)	10 minutes
40°C (104°F)	3 minutes
50°C (122°F)	1.5 minutes

Dry-to-Tape time:

Experimental procedure: Panels were knife coated with the Dual Cure formulation at a thickness of 3 mils and allowed to stand at room temperature for 15 minutes to allow for solvent flash. The panels were placed on the thermostated platen and exposed to the Super Diazo Blue lights for various lengths of time. Strips of 3M ScotchTM #250 tape were

placed on the panels immediately after taking out from under the lights and for every 30 minutes thereafter for up to 3.5 hours. Dry-to-tape time (a.k.a. "resistance to marring by tape") was determined using the procedure spelled out in BMS 10-60 section 8.2.7.

Results:

Platen Temperature	Exposure Time	Dry-to-Tape Time
30°C (86°F)	10 minutes	1.5 hours
30°C (86°F)	15 minutes	1.5 hours
50°C (122°F)	2 minutes	2 hours
50°C (122°F)	4 minutes	immediately out from lights
50°C (122°F)	8 minutes	immediately out from lights
50°C (122°F)	15 minutes	immediately out from lights

Minimum dose required for rapid (< 1 hour) dry-to-tape:

$$\begin{aligned}
 \text{Dose} &= \text{Intensity} \times \text{Time} \\
 &= 4.99 \text{ mw/cm}^2 \times 240 \text{ sec} \\
 &\sim 1.2 \text{ J/cm}^2
 \end{aligned}$$

TASK 2: DEVELOP DUAL CURE EPOXY/ACRYLATE AEROSPACE PRIMERS

The goal of this task was to develop a dual cure epoxy/acrylate aerospace coating which meets the performance requirements of existing solvent borne epoxy primers. Current materials are qualified under one of three specifications: MIL-P-23377 "Primer Coatings: Epoxy, Chemical and Solvent Resistant" for conventional hydrocarbon solvent coatings; MIL-P-85582 "Primer Coatings: Epoxy, Waterborne" for water reducible coatings; or Boeing Materials Specification (BMS) 10-79 "Urethane Compatible Corrosion Resistant Primer" for commercial aircraft coatings. The key requirements for each of these specifications are summarized in Appendix 2. Four sub-tasks were proposed for the epoxy/acrylate coating task, which parallel Task 1 in organization. However, Boeing Defense and Space Group was not a partner in the Task 2 testing.

Sub-task 2.1 – Select and prepare suitable substrates for testing.

Sub-task 2.2 – Optimize and screen coating formulations using a series of tests selected from the various qualification standards.

Sub-task 2.3 – Perform testing of selected formulations using a wider range of the qualification standards.

Sub-task 2.4 – Determine and optimize application and cure techniques for the dual cure epoxy/acrylate compositions.

Work in the first six months of the contract resulted in completing the identification and preparation of suitable substrates and identifying a series of screening tests for initial evaluations of primers relative to the military and commercial specifications referenced above. A baseline formulation was developed. However, this baseline formulation did not provide reliable cure. The focus of the second six months of the contract was on identifying and understanding the underlying cause of the unreliable cure in this system. During this period it was determined that the cure behavior was the result of moisture inhibition. The effect of relative humidity and temperature on cure of the epoxy/acrylate primer formulations was quantified. From this work it was determined that acceptable cure was achievable at relative humidity values less than 50%. However, acceptable cure could only be achieved by heating to 40°C when the relative humidity was above 50%. During the third six months of the contract, 3M requested that Task 1 receive priority over the primer development of Task 2. This was because of cure reliability difficulties,

the status of the urethane/acrylate topcoat development at that time, and the greater potential it represented in terms of reduction in both solvent emissions and energy usage in the aerospace coating industry.

Furthermore, the need for non-chromated primers had risen as a result of increased disposal problems associated with chromates and other heavy metals. The development of a non-chromated primer was outside the scope of the original contract and would have required considerable effort to accomplish. Consequently, further effort on the development of a dual cure aerospace primer was halted with Doe concurrence.

Sub-task 2.1: Select and Prepare Substrates

Two types of test panels were obtained and used: Bare aluminum without surface-treatment (Q-panels) and alodine treated 2024 aluminum panels (chromate anodized). Primed aluminum panels obtained from Boeing (prepared using a MIL-P-85582, waterborne epoxy primer over 2024 T3 aluminum) were selected as the control to provide a comparison standard for the dual cure primer development under this task. The various primer specification documents provide explicit guidance for surface preparation of panels for each of these tests. 3M performed the majority of the screening tests using bare aluminum panels and followed up with alodine panels as required.

These data indicate how the rate of cure, and hence the set-to-cotton and dry-to-tape times, are dependent on both the light intensity and temperature. Within the range evaluated, it appears that temperature has a greater influence on the set-to-cotton time and both intensity and temperature have a strong influence on the dry-to-tape time.

Sub-task 2.2: Optimize and Screen Coating Formulations

A series of screening tests were identified for performing initial evaluations of primers relative to the military and commercial specifications. These tests were selected to allow rapid assessment of coating performance and evaluation of the impact of formulation changes. The screening tests proposed were: pencil hardness; wet and dry tape adhesion; impact flexibility; cold temperature bending; Skydrol hydraulic fluid resistance; distilled water resistance; salt spray resistance; and filiform corrosion resistance. In addition to these tests, VOC levels were routinely measured to assure that adequate cure was being achieved.

As a starting point for the epoxy/acrylate primer development, literature sources were surveyed to determine a typical primer formulation. A MIL-

P-23377 conforming primer formulation was reported by Hegedus, et al, in the Journal of Coating Technology, volume 61, number 778, November 1989 as shown below:

Component A:	
Epoxy Resin (Shell Epon 1101-T75)	18.2%
Strontium chromate	12.0
Titanium dioxide	2.3
Magnesium silicate	5.5
Silica	2.9
Cellosolve acetate	16.4
Methyl ethyl ketone	4.1
Component B:	
Polyamide resin (Henkek Versamid 115)	7.5%
Isopropanol	24.5
Toluene	6.6
<hr/>	
100.0%	

This formulation consists of 25.7% resin, 12.0% chromate (for corrosion inhibition), 2.3% TiO₂ (for hide), 8.4% fillers, and 51.6% solvent. Converting this to a solventless formulation results in 53% resin, 25% chromate, 5% pigment (TiO₂), and 17% fillers. Based on earlier work done using epoxy/acrylate formulations, a starting resin formulation consisting of a single epoxy resin and both monofunctional and difunctional acrylates was selected as shown below:

25%	Chromate (BaCrO ₄)
70%	Resin, consisting of
	60% Epoxy 1
	40% Acrylates
	90% Monoacrylate 1
	10% Diacrylate 5
5%	Pigment (TiO ₂)
0.5%	Iron photocatalyst (CpFeXylSbF ₆)
0.6%	Dispersant 5 (2% of chromate + pigment)
0.6%	Co-catalyst 1 (2% of acrylate resin)

This formulation provided the same levels of chromate and pigment as the published formulation, adjusted for solvent. From previous epoxy/acrylate work it was known that a higher level of iron

photocatalyst, 0.5% based on resin, was needed for epoxy systems compared to the urethane/acrylate formulations, and that the SbF_6^- counterion provided better performance than the PF_6^- counterion. Both strontium chromate and barium chromate are usually used for corrosion inhibition. Preliminary experiments with various epoxy/acrylate formulations had indicated that strontium chromate containing formulations provided significantly poorer cure due to absorption of light by the strontium chromate. This absorption prevented efficient activation of the photocatalyst.

Test panels coated with the above formulation did not cure well at either 0.5 or 3.0 mil thicknesses and illuminated for 15 minutes with quartz/halogen lights. The 3 mil coatings did become tack-free, but were still quite soft. Repeating this experiment with lower levels of chromate and pigment improved the cure of the resin. At 14.5% BaCrO_4 and 2.9% TiO_2 , cure was observed with 10 minute exposure to quartz/halogen illumination. The cure appeared to continue after removal from the light source as evidenced by additional increase in pencil hardness over time. Immediately after illumination the hardness was 4B, two hours later the hardness has increased to 2H, and ultimately a final hardness of 4H was achieved. The VOC measured for this sample was 5.1% weight loss, based on the resin, and the reverse impact was less than 20 in.-lbs. Based on the results obtained on these preliminary experiments, the primary concern identified for the epoxy/acrylate formulations was obtaining adequate cure in the presence of chromate and pigment.

A series of experiments were performed by adding only chromate or only pigment to the resin formulation identified above. The purpose of these experiments was to determine the individual effect of each component on the degree of epoxy/acrylate cure obtained. In both experiments, the samples were cured under Super Diazo Blue Bulbs for 15 minutes and then measured for VOC level. Elevated levels of either BaCrO_4 and TiO_2 were found to have a negative effect on the epoxy/acrylate cure. Acceptable cure was obtained at levels of BaCrO_4 below 10% or TiO_2 levels below 5%.

A comparison of various monoacrylates in unpigmented, unchromated epoxy/acrylate samples was also performed to determine if the cure could be improved by changing the monoacrylate selected. Based on this comparison, no change to the monoacrylate was made. Monoacrylate 1 provided the best VOC performance. Monoacrylate 2 provided slightly poorer VOC levels with similar to slightly improved functional performance. The detailed results from the chromate and pigment level

experiments as well as the comparison of various monoacrylates are contained in the First Semi-Annual Report (DE98001352).

In addition to resin, chromate, and pigment, fillers are frequently added to the primers to provide inert materials and reduce cost. The initial formulation tested was noted to be too low in viscosity for flow properties when sprayed. A preliminary screening of possible fillers was accomplished using published data from "The Pigment Handbook, Volume I, Properties and Economics", Peter A. Lewis editor, Second Edition 1988, John Wiley & Sons. Based on this information, several different fillers were evaluated for their effects on cure of the epoxy/acrylate primer. The results from these experiments indicated that epoxy silane treated kaolin did not significantly interfere with the epoxy/acrylate cure at levels as high as 40 wt-%. Formulations were prepared with combinations of kaolin and BaCrO₄ at various levels and coated and cured under Super Diazo Blue Bulbs. Formulations at 10% BaCrO₄ or higher were found to not cure well.

In addition to the above experiments, which focused primarily on the effect of specific single components on the cure of the epoxy/acrylate formulation, a range of formulations was prepared using various combinations of chromate and fillers with the 60% epoxy/40% acrylate resin system. Increasing the viscosity of these formulations by changing the filler or adding thixotropes was also evaluated. Incorporating thixotropes into the formulations was found to result in air entrapment and cure inhibition. Talc and silica were found to provide increased viscosity and acceptable cure without BaCrO₄ present. Formulations containing chromate, filler (either kaolin or Zeeospheres), and talc did not cure while formulations containing only filler and talc provided significantly better cure.

By the end of the first six months of the contract, it had been determined that the baseline formulation was not providing reliable cure. A range of filler types and levels had been examined, but no clear pattern was established. Surface effect of the filler, particularly silane treatment, appeared to have a positive effect on cure. However, the problem of obtaining reliable cure for the epoxy/acrylate primer formulation remained largely unsolved. Formulations containing only chromates (at less than 10%), only pigment (total, at less than 5%), or only filler appeared to cure well. However, formulations containing all of these materials did not provide acceptable cure. Furthermore, the viscosity of the baseline formulation was too low, giving rise to runs and sags on application. Attempts to increase the viscosity of the formulation by

adding a thixotrope were unsuccessful because of problems with air entrainment. The focus of the effort turned to identifying and understanding the underlying cause of the unreliable cure in this system.

The effect of fillers on the cure of epoxy/acrylate formulations was examined. The effect of filler type and concentration on measured VOC level of samples cured for 15 minutes under Super Actinic Bulbs was determined. From these results, it was concluded that when added individually these fillers had the following effects on cure. Mica and granular silica were found to strongly interfere with the epoxy/acrylate cure. At 5% added mica, VOC levels increased approximately 1.7% and at 10% added mica, no cure was observed. Addition of talc provided good cure at the 10% level, but essentially no cure at loadings above 20%. Fumed silica could be added at levels up to 5% with good cure. Barium sulfate provided good cure up to approximately 18% and chlorite provided good cure up to 10%. Both of these fillers showed inhibition of epoxy cure at higher levels. Zeospheres provided good cure up to at least 30%.

An evaluation of silane surface-treatment on kaolin was previously identified and reported to significantly improve the cure of the epoxy/acrylate formulations. The effect of silane treatment on fumed silica and mica was examined. The silane treatment appeared to have an advantageous effect on reducing the cure inhibition with fumed silica. However, no improvement was observed with silane treating mica. It was found that adding the silane to the pigment resin system, instead of pre-treating the filler with silane before dispersing it in the resin system, provided similar VOC levels as the pre-treated fillers.

The effect of different types of TiO_2 on epoxy/acrylate cure was evaluated. The TiO_2 (R-960) used in the baseline formulation is the same as the pigment in the urethane/acrylate topcoat formulation. This material is surface-treated to provide better weathering performance, but the results of tests with other TiO_2 pigments suggest that the surface-treatment is negatively affecting epoxy cure. All four of the other TiO_2 pigments evaluated gave better epoxy cure as determined by lower VOC levels.

A test was developed for detecting absorption of activated catalyst (free iron) on the surface of fillers using calorimetric indicators. Previous tests with silane surface-treated kaolin had shown good cure. Untreated kaolin was found to gel the epoxy/acrylate formulation. This was attributed to strongly acidic, active sites on the kaolin surface. Additional analytical experiments demonstrated that the mechanism for

cure inhibition by the various fillers was related to surface adsorption of the active catalyst. It was found that the use of silane treated fillers significantly reduced surface adsorption of the catalyst and therefore minimized the cure inhibition by the fillers.

Several experiments were conducted on epoxy/acrylate formulations with barium chromate and various fillers at different iron photocatalyst levels. The amount of catalyst required to achieve good cure was determined to be dependent on the amount and type of fillers in the formulation. At 10% barium chromate, 1.0% photocatalyst resulted in good cure. However, at 20% barium chromate, 1.5% photocatalyst was needed to achieve good cure. Higher filler loadings and the addition of pigment resulted in insufficient cure even at photocatalyst levels as high as 2.0%.

The effect of relative humidity and temperature on cure of the epoxy/acrylate primer formulation was evaluated by measuring tack-free time and VOC emissions for clearcoat samples. A controlled temperature platen was constructed which allowed heating the test panels during cure. Samples were cured at room temperature ($\sim 22^{\circ}\text{C}$), 30°C and 40°C and relative humidity variations from 37 to 62%. Acceptable cure rates were achieved at all temperatures evaluated at relative humidity below 50%. Tack-free time ranged from 2.5 minutes to 60 minutes. However, acceptable cure rates could only be achieved by heating to 40°C when the relative humidity was above 50%.

As a potential means around the unreliable cure experienced with epoxy/acrylate primer formulations, several epoxy based formulations without acrylate were evaluated. Formulations were prepared with epoxy/acrylate and epoxy only resin systems with 10% R-700 TiO_2 , 20% Barium Chromate, and 15% silica. Both formulations contained 2 wt-% iron photocatalyst and 0.8 wt-% Co-catalyst 1 based on the resin. Sample panels were coated with the two formulations and photolyzed for 15 minute. The epoxy resin system demonstrates no weight loss due to the fact that the epoxies continue to cure once the cationic polymerization has been initiated. On the other hand, if the acrylate component of an epoxy/acrylate system is not fully cured before the lights are turned off, no further cure will occur in the absence of light.

Even though the epoxy formulation had no measurable VOC value, the reverse impact performance was well below the required value. A resin system based on Epoxy 1 and Flexibilizer 1 was evaluated to try to improve reverse impact performance. The resulting samples had only slightly higher reverse impact values (~ 30 in-lb as compared to 10 in-lb).

However, reverse impact on a pure Epoxy 1 coating, with no fillers, revealed that reverse impact values of 80 in-lb were achievable. These results suggested that improved dispersants were required in the filled epoxy primer formulations.

Dispersants 1, 7, 8, and 9 were evaluated on BaCrO₄ in Epoxy 1 mixtures. Dispersant screening involved determining Brookfield viscosity as a function of dispersant loading. Dispersant 1 was determined to reduce the viscosity the greatest amount and to maintain the lower viscosity over a broad loading level. Formulations were prepared with 10% R-700 TiO₂, 20% BaCrO₄, and 15% silica in Epoxy 1 both with and without Dispersant 1. Both formulations were observed to only skin over after a 15 minute photolysis step. Full cure was not achieved until the following morning.

The lack of through cure in the above described formulations was suspected to be due to the strong absorption of the visible light by the BaCrO₄, resulting in the iron photocatalyst not being fully activated through the thickness of the coating. Several other iron based photocatalysts which were measured to have stronger visible light absorption than the catalyst currently being used were evaluated. No significant improvement in cure performance was observed.

Several non-chromated corrosion inhibitor pigments were evaluated. Commercially available surface modified zinc phosphate was dispersed at a 15% level in Epoxy 1 and resulted in a mixture which gave good grind. This formulation cured tack-free in less than 1 hour with 2% photocatalyst. Commercially available barium metaborate was dispersed at a 15% level in Epoxy 1 and also gave good grind; however, some foam formation was observed. This formulation cured tack-free in 31 minutes with 2% photocatalyst. Both of these formulations gave fairly good cure performance when compared to a non-pigmented epoxy coating which cured tack-free in 12 minutes. Aluminum zinc phosphate was dispersed with barium sulfate, titanium dioxide, and either talc or Zeospheres in Epoxy 1. A 39% pigment loading was achieved in the formulation containing talc, while a 50% pigment loading was achieved in the formulation containing Zeospheres. Both formulations cured well but were found to have very low reverse impact performance (~10 in-lb).

The effect of several polyols (added as flexibilizers) blended with Epoxy 1 was evaluated in unfilled formulations. The polyols were found to reduce the T_g of the cured coating, as anticipated, from an initial value of approximately 90°C to values ranging from 30 to 60°C, depending on the

polyol used and the ratio of polyol to epoxy. However, the polyols also reduced the hardness of the cured coatings with no significant improvement in impact performance. It was also found that when fillers were added to the epoxy without polyol, the Tg decreased from 90°C, with no fillers to 60°C at 30% pigment volume concentration and 40°C at 50% pigment volume concentration, using a standard pigment mixture. This decrease in the epoxy Tg is probably the result of inhibition of the epoxy cure caused by the pigment being present.

At this point in the contract, 3M requested that Task 1 receive priority over the primer development of Task 2, due to cure reliability difficulties and due to the status of the urethane/acrylate topcoat development and the greater potential it represents in terms of reduction in both solvent emissions and energy usage in the aerospace coating industry. Furthermore, the need for non-chromated primers had risen as a result of increased disposal problems associated with chromates and other heavy metals. The development of a non-chromated primer was outside the scope of the original contract and would have required considerable effort to accomplish. Consequently, further effort on the development of a dual cure aerospace primer was halted with DoE concurrence.

TASK 3: DEVELOP SOLVENTLESS TAPE BACKING

The goal of this task was to evaluate the use of dual cure catalysts in saturating resins for tape backings. The properties of the dual cure catalyzed backings were compared to the performance of similar, commercial materials using conventional solvent based technology. Five sub-tasks were performed for the tape backing effort:

Sub-task 3.1 – Select a suitable tape backing substrate from a list of possible alternatives.

Sub-task 3.2 – Determine the optimal resin formulation using laboratory scale experiments.

Sub-task 3.3 – Establish optimal curing condition with the desired resin formulation.

Sub-task 3.4 – Prepare samples of a completed pressure sensitive adhesive tape using the dual cure catalyzed backings.

Sub-task 3.5 – Evaluate the properties of these experimental tapes compared to U.L. and internal 3M specifications for electrical tape performance.

Sub-Task 3.1: Select Tape Backing Substrates

Several substrates were saturated and evaluated for use as tape backings. Criteria used for selecting a backing included obtaining the proper adhesion between the saturating resin and the backing. The electrical and mechanical properties of the coated backing were also measured to determine the appropriate backing. The following substrates were saturated with U.V. curable epoxy solution:

- Polyester film
- Non-woven polyester film
- Glass cloth
- Cellulose acetate cloth
- Paper (crepe and flat back)

In the case of polyester films, different types of treated films were evaluated in order to obtain the proper adhesion between the epoxy and the backing. The five films chosen for this study were:

1. Unprimed film
2. Corona treated film
3. Primed film A
4. Primed film B
5. Primed film C

The films were coated and cured with epoxy solution and adhesion values were determined on these films. Polyester film which had been specially treated for epoxy adhesion provided the best performance followed by corona treated film. The coated backings were also post-cured at 120°C for 2,4,6 and 8 minutes and subsequently the adhesion values were determined. No increase in adhesion was observed as a result of a post-cure treatment.

The conclusion from this study was that the dual cure epoxy solution can be used with any backing needing a saturant to modify either the electrical or mechanical properties of the backing. In the case of polyester film, either specially primed or corona treated film was needed to obtain adequate adhesion between the cured epoxy and the film.

Sub-task 3.2: Determine Resin Formulation

Several different formulations were prepared depending upon the application and the type of substrate used. The typical formulation contained the following:

- Base epoxy resin
- Flexibilizer
- Brominated epoxies (for flame retardancy)
- Pigments
- Fillers
- Flame retardant agents (antimony oxides)
- Iron photocatalyst (CpFeXylSbF_6)
- Co-catalyst

Different photocatalyst concentrations were evaluated in order to identify the amount needed to provide adequate cure in acceptable time periods. It was concluded that 1% photocatalyst was the optimum concentration for the conditions used in the laboratory (1% based on the weight of epoxy). The addition of the co-catalyst was also found to increase the curing rate, as determined by Differential Scanning Calorimetry (DSC), and hence was used in all the formulations.

The flexibilizers were used at different concentrations depending upon the backing and the desired amount of flexibility. Increasing the amount of flexibilizer resulted in increased flexibility (i.e. lower modulus and higher elongation) and reduced hardness and tensile strength. From the data reported in the Second Semi-Annual Report, it can be seen that the concentration of flexibilizer has a significant effect on the mechanical properties of the backing. This phenomenon can be utilized to vary the backing properties over a broad range of values. Formulations containing Flexibilizer 1 generally resulted in substrates with an odor. The backing was analyzed for the odor causing component but it was difficult to arrive at any conclusions from the analysis. Flexibilizer 2 produced backing with no odor and consequently was the preferred flexibilizer in most of the formulations.

Flame retardant formulations were prepared with Brominated epoxy and antimony oxides. To optimize the formulation, the effect of the ratio of the two flame retardant components on the flame test was studied. Samples with three different ratios of Br/Sb (the active flame retardant components) were prepared: 4.5, 3.0 and 1.15. U.L.-510 flame test was performed on the backings prepared from the above formulations containing the different ratios of the flame retardant additives. There was some difference in the flame time for the three formulations, but all of the samples passed the U.L.-510 flame test, which specifies a 60 second maximum flame time. It was concluded that a ratio of 4.5 would be utilized since it contains the least amount of antimony trioxide.

Antimony pentoxide was also evaluated, since it is perceived to be a safer additive compared to antimony trioxide. Several formulations were prepared and cured with different levels of antimony pentoxide. Unfortunately the formulations containing antimony pentoxide did not seem to cure as rapidly as the antimony trioxide formulations. The impurities in antimony pentoxide (commercial sources contain only 55-65% antimony pentoxide) seem to hinder the curing mechanism of the iron photocatalyst. Therefore antimony trioxide was utilized in those formulations requiring flame retardancy.

The effect of the pigments on the formulations was also studied. Three different pigments were evaluated: black, yellow and white. The pigments were pre-dispersed in the epoxy and hence no problem with pigment dispersion was encountered. The backings were coated and cured with formulations containing the pigments. The pigments did not affect the cure and films of good quality were obtained from these formulations.

Sub-task 3.3: Establish Curing Conditions

The formulations prepared in the laboratory were coated and cured in a laboratory U.V. processor specially designed for this purpose. A flow diagram of this unit is shown in the Second Semi-Annual Report. The unit consists of a coating station, U.V. curing unit and a winding station. The coating station can be modified to suit the coating operation without much difficulty. The U.V. processor is equipped with a variable intensity lamp with three different intensity settings. The winding station is controlled by a variable motor which controls the speed of the coating operation.

Several experiments were conducted to determine the optimum method of curing. Since the coating operations could be carried out at different speeds and different lamp intensities, an experiment was conducted which was designed to result in a backing which could be coated and fully cured as fast as possible. A glass cloth backing was coated and cured at 300 watts/inch intensity and three different speeds (4.6 ft/min, 9.7 ft/min and 15.7 ft/min). The samples were then characterized by differential scanning calorimetry (DSC) to determine the T_g (glass transition temperature) of the cured samples. There was very little difference in the T_g values of the three different samples coated and cured at different speeds, indicating that all of the samples were cured to essentially the same degree. This indicates that the epoxy solution can be cured at high speeds without sacrificing the degree of cure.

To monitor the cure, a simple test was developed to determine the degree of cure. This test is based on wet chemistry utilizing a Bromophenol blue solution. This test was evaluated with several samples and seems to provide a qualitative indication of the degree of cure. This technique should prove to be useful as a quality assurance procedure in manufacturing.

The shelf-life of the formulation is an important criteria for production coating operations. Most of the current thermally cured epoxy solutions have a short shelf-life after the two parts have been mixed. One advantage of the U.V. cured epoxy solutions is the shelf-life that they have. Several sample formulations were stored and the viscosity monitored over a period of time. No appreciable change in viscosity was observed after approximately 9 months.

The effect of post-curing at elevated temperature on mechanical properties of the backing was also evaluated. Polyester film samples

were coated either one-side or both sides with an epoxy solution, cured on the laboratory U.V. processor, and post-cured at 120°C in an oven for 2, 4, and 6 minutes. Tensile and elongation were measured on the films and compared to a control film which was not post-cured. There was no noticeable change in the mechanical properties as the result of post-curing and hence it was concluded that no post-curing is necessary.

The effect of coating thickness on the mechanical and electrical properties of the backing was also evaluated. Two formulations were prepared and coated on a non-woven polyester backing. The coating was varied from 4.5 to 8.0 mils. The cured backing was then characterized for tensile, elongation and dielectric strength. A coating of 6 mils seems to give the proper balance of the properties. The backings were also post-cured at 100°C for 10 minutes and then tested for the above properties. The results of these experiments are summarized in the Second Semi-Annual Report.

Sub-task 3.4: Prepare Pressure Sensitive Adhesive Tape

Tapes were prepared by coating the saturated backings produced on the laboratory scale U.V. processor with one of two different adhesives. A rubber based adhesive was coated at a 3M pilot plant. An acrylic adhesive was coated by a transfer process and was done using small strips of the backing.

The first scale-up of the tape backing formulation was performed at the 3M Hartford City, Indiana plant in February, 1992. The epoxy solution was prepared in a large reactor producing about 1500 lbs of the resin. About 4000 yards of polyester film and non-woven polyester film was coated at speeds ranging from 100 to 200 ft/min with four U.V. lamps. The polyester backing which was coated on both sides with the epoxy solution during this trial blocked upon sitting. The cause of this behavior was identified and can easily be avoided in the future. The experiments were highly successful and the simple process of coating and curing the epoxy solution was demonstrated.

A second scale-up experiment was conducted in St. Paul, Minnesota. Several coating methods were evaluated using epoxy solutions of different viscosities. Several different coating techniques were identified which can be used to coat these solutions at production speeds.

Sub-task 3.5: Evaluate Tape Properties

Several rolls of tapes, produced in the laboratory, were tested for standard tape properties and compared to the existing products. The results indicate that the performance of these tapes are quite similar to the standard tapes in most cases and should be accepted without any problem.

The following tests were performed on the tapes according to the 3M or ASTM specifications.

- Tensile
- Elongation
- Two Bond test
- Adhesion
- Dielectric Strength
- Flame Test (on flame retardant formulations)
- Insulation Resistance
- Electrolytic Corrosion
- Solvent Resistance

The effect of the flexibilizer on the final tape properties was studied. Four different formulations with varying amounts of the flexibilizer were prepared and cured. The backings were coated with a rubber based adhesive and in some cases with an acrylic adhesive. The rolls of tapes were then characterized and the results are reported in Tables 3.1 and 3.2.

Table 3.1: Backing properties produced from dual cure epoxy saturant with different concentration of Flexibilizer 1.

Backing	Epoxy 1 (parts)	Bromi- nated Epoxy (parts)	Flexibili- zer 1 (parts)	Thickness (mils)	U.L.-510 (secs)
A	40	30	30	5.2	<20
B	50	30	20	5.1	34
C	60	30	10	5.1	23
D	70	30	0	5.4	13

Table 3.2: Performance properties of tapes produced from dual cure backings saturated with different concentration of Flexibilizer 1 and coated with either rubber based or acrylic based adhesive.

Backing	Adhesive	Tensile (lb/in)	Elong. (%)	2-bond (Oz/in)	Adhesion (Oz/in)	Dielectric (kV)	Resist. (ohms)
A	rubber	33	25	102	36	4.96	2.0E10
B	rubber	34	25	128	39	4.67	3.3E11
C	rubber	33	13	122	42	4.93	2.9E12
D	rubber	34	4	122	39	5.07	1.2E13
B	acrylic	34	26	97	45	5.70	
C	acrylic	33	14	88	45	4.26	

The physical and electrical properties of various backings coated with a rubber based adhesive were also measured and are reported in Tables 3.3 and 3.4.

Table 3.3: Physical performance properties of tapes produced from dual cure backings and rubber based adhesive along with control tape samples.

Backing	Formulation	Tensile (lb/in)	Elongation (%)	Adhesion to Steel (Oz/in)	#2 Bond (Oz/in)
Non-woven Polyester	50/30/20	34	7	26	96
	control	40	27	50	130
Flat-Back Paper	50/30/20	51	11	ruptured	106
	control	44	7	38	140
Crepe Paper	75/0/25	31	14	40	68
	control	24	10	27	98

Table 3.4: Electrical performance properties of tapes produced from dual cure backings and rubber based adhesive along with control tape samples.

Backing	Formulation	Insulation Resistance (Megaohm)	Electrolytic Corrosion	Dielectric Strength (Volts)
Non-woven Polyester	50/30/20	14.6×10^{14}	0.98	6280
	control	10.4×10^{14}	1.00	6640
Flat-Back Paper	50/30/20	$>10^{14}$	0.71	1800
	control	$>10^{14}$	0.72	2100
Crepe Paper	75/0/25	$>10^{14}$	0.78	2480
	control	9.0×10^{13}	0.63	2740

In most cases, the properties of the tapes produced from dual cure backings are comparable to the control products currently being made by the solvent based process, and the advantage of the U.V. process is the ease of the preparation of the backing. The control tapes which were tested for comparison purposes were made in the factory with much greater uniformity than the laboratory produced backings. The properties of the dual cure backings would be better when made in a factory process environment and compared to the standard products.

TASK 4: EVALUATION OF THE DUAL-CURE PROCESS

The experience gained throughout the contract was used to evaluate the performance of the dual cure process. The evaluation was conducted in two parts. First, a generalized evaluation was made where suitability for particular markets will be judged. This was followed by an evaluation of the actual commercial applications chosen for demonstration in Phase III of the contract. These evaluations were based upon the technical performance determined over the course of the contract, as well as a comparison of the process economics with competitive technologies. A similar analysis of energy savings was performed for a generic coating process, as well as a specific analysis of the actual Phase III demonstration applications. Calculations of total energy savings in the U.S. economy in 2010 which are expected due to implementation of the dual cure process were also updated.

Sub-task 4.1: Evaluation of Technical Performance

At this point in the development of dual cure technology, several distinct advantages and disadvantages are apparent. These factors will influence the probability of success in any given application. Dual cure does make available materials having a wide range of physical properties. Often, combinations of properties are possible which are not readily accessible using existing techniques. The technology is still in the process of evolving, and based on past experience, we expect further improvement to occur.

Additional pressure for the adoption of dual cure comes from the increasing regulation of solvent emissions. In many industries, reduction of VOC (volatile organic compound) emissions has become a major priority. Targeting dual cure development toward these industries may improve the chances for its adoption. Applications requiring very high performance standards, combined with low VOC emissions, are particularly suited to further development. Because of the inability of conventional solventless techniques to meet their physical property needs, these industries may be more willing to adapt to the requirements of a photocuring process. In addition, demonstration of success in applications with such demanding requirements may more readily convince other industries to investigate dual cure as a solution to their coating problems.

The major advantages of the dual cure process which have been identified to date include the following:

Physical Properties - Often, when the performance of a dual cure formulation is compared to its separate components, the dual cure material is found to be superior to either component alone. Dual cure materials often combine the best aspects of both components, giving a combination of properties superior to either. This is most evident with the tensile properties. The ability to maintain most of the tensile strength of the stronger component, and simultaneously maintain the elongation properties of the higher elongation component, results in materials with exceptional toughness. Increased toughness is reflected in other properties such as the ability to withstand a bend or an impact. The ability to combine properties in this way is a function of the molecular structure resulting from dual cure. When two different multifunctional monomer types polymerize simultaneously, but independently from each other, a structure known as an interpenetrating polymer network, or IPN, may result. Each monomer type forms its own crosslinked network independently from the other. The two networks are not significantly interconnected by chemical bonds, but are prevented from separating by the entanglement of the two networks. The property enhancement observed is a result of this type of structure. IPNs may be prepared in other ways, but the dual cure process is particularly advantageous from a processing standpoint.

Low-VOC Formulation - Due to viscosity requirements imposed by various application techniques, coatings are often applied as solutions in volatile solvents. Most commonly, this is done to reduce the viscosity of the formulation to a level which is suitable to the application method. It is difficult to use high viscosity compositions for the application of very thin films, or when spraying is the preferred mode of application. Addition of high levels of fillers or pigments further increases the problem. After application, the solvent is removed, either by air drying, or forced drying in an oven. Emission of these solvents to the environment is a concern, and is being increasingly regulated. Several solutions to this problem are possible. Recovery or incineration facilities designed to remove solvents from the air stream of conventional coating processes have been designed and are in use. These tend to be expensive and energy intensive to operate and are often viewed as an interim solution to the problem. Modification of a process to eliminate solvent use is preferred to solvent recovery when it is possible to do so without adversely affecting the properties of the coated article. Several approaches have been investigated in industry to eliminate solvents. One approach is to use water as a viscosity reducing diluent. Not all cure chemistries are water compatible, however. In addition, many of these compositions still contain appreciable levels of co-solvents, since water by itself is not the

best solvent for many organic coating compositions and solvents are often necessary for good film formation. Many water based systems also suffer from a reduction in physical properties as compared to their solvent containing equivalents, especially at the high end of the performance/appearance spectrum. Variation of properties with the relative humidity during cure is also commonly seen, since this effects the relative evaporation rates of the water and co-solvent portions of the coating and may effect the extent of water reaction in reactive systems such as 2-part polyurethanes. An alternative approach, and the one used in the dual cure process, is the addition of a reactive diluent. These are relatively low molecular weight, low viscosity monomers which are substituted for all or part of the solvent in a formulation. Unlike solvent, they participate in the cure process, and are incorporated in the final cured material. Cure may occur by a photochemical process, or thermally. A common example of the use of a reactive diluent is the addition of styrene to unsaturated polyester resins to decrease viscosity. In the dual cure process, the acrylate portion of the formulation serves this viscosity reducing role. The need for viscosity reduction is greatest in urethane systems, since the urethane precursors are generally of high viscosity. Unlike most systems using reactive diluents, the properties of the materials made with dual cure can actually be improved over comparable compositions not containing the acrylate portion. The ability to improve the coating process, and simultaneously improve the properties of the cured film, make dual cure an attractive method of solvent elimination. The amount of solvent which can be replaced with acrylate monomer depends mostly on the method by which the coating is applied. For web coating applications, viscosities of several thousand centipoise are desirable, and in most cases, solvent can be eliminated entirely. For spray application, viscosities in the area of 100 centipoise are needed to achieve good atomization, and in most cases some solvent will be required. In many spray applications, solvent loss is also required to achieve rapid viscosity build-up on the substrate. This prevents running and sagging once the film has been applied.

Use of Visible Light Sources - A major concern preventing more widespread adoption of photocuring methods is the use of ultraviolet light sources. Due to health concerns, worker exposure to ultraviolet light must be avoided. This has limited the use of radiation curing to applications where the light source can be well shielded, such as industrial coating lines. Catalyst compositions have been devised which now allow the use of visible light in the curing of dual cure compositions. This should assist in the adoption of photocurable coatings in a wider variety of applications, such as batch coating applications where light

shielding is not always practical. For applications not requiring visible light use, such as unpigmented films coated on a web, high intensity ultraviolet lamps may still be used. The higher lamp intensity, combined with greater catalyst absorption in the U.V., will allow shorter cure times and faster line speeds than with a visible lamp source. The ability of the catalyst to function with either light source provides the processing flexibility to adapt dual cure to a variety of applications.

Cure of Pigmented Systems - A disadvantage encountered with many photocuring processes is the inability to cure heavily pigmented compositions. This results from the fact that many of the most common pigments absorb ultraviolet light at the same wavelengths required for catalyst activation. Titanium dioxide, the most common white pigment, for example, absorbs strongly throughout the ultraviolet up to 400 nm. The iron catalysts used in the dual cure system also have strong absorption in the ultraviolet. In addition, however, they also absorb weakly in the blue region of the visible spectrum. Many of the pigments such as titanium dioxide, which are regularly used at very high levels in pigmented compositions, are reasonably transparent to light in this wavelength region. Pigmented compositions can therefore be cured with the dual cure catalysts using visible light. This is similar to the approach used in the past to develop photoinitiators for acrylate polymerizations. These catalyst systems have absorption spectra which are very similar to the dual cure catalysts. The dual cure catalysts have the added advantage of allowing cure of the urethane and epoxy monomers in the presence of pigments. Catalyst combinations have also been developed which allow efficient cure of acrylates combined with epoxies or urethane precursors, using visible light. Cure of coatings containing a variety of pigment colors has been demonstrated. In addition to white, colors which have been cured include black, blue, red, green and yellow. All cured at rates comparable to white, with the exception of red which cured more slowly. This was expected due to competitive absorption of the blue light by the red pigment. Lamps which have output concentrated in the desired blue portion of the spectrum are commercially available for use in blueprint machines. The emission of these lamps has been optimized for the diazo blueprinting dyes, which have absorption spectra similar to the dual cure catalysts.

No Inerting Required - Compositions have been developed in both the urethane/acrylate and epoxy/acrylate systems in which the acrylate portion cures in air. In conventional acrylate curing, the free radical cure is inhibited by oxygen. This results in incomplete cure and inferior properties. This can be partially overcome by use of highly functional,

high molecular weight acrylates where a crosslinked network is established at low conversions, but these materials have higher viscosities than we require for solvent replacement. For low molecular weight, primarily monofunctional acrylate such as the ones we are using, polymerization of the pure acrylate does not occur in air. As a result, most radical cured acrylate polymerizations are done under a nitrogen atmosphere. In the dual cure systems, acrylate cure appears to be slowed by oxygen inhibition, but goes substantially to completion. This is due to the formation of the epoxy or urethane network, which slows oxygen diffusion into the film, allowing acrylate cure to take place. This allows the elimination of nitrogen use, and its associated expense. For applications requiring fast acrylate cure with very low levels of residual acrylate monomer, nitrogen inerting may still be used to enhance acrylate cure.

Cure of Thick Films - A problem encountered when using catalysts such as the triarylsulfonium salts for the cationic cure of epoxy monomers is the inability to cure thick films. This is due to the inability of ultraviolet light to penetrate deep into the coating, because the activated catalyst absorbs light in the same range as the unactivated catalyst. Most of the light is absorbed near the film surface, and underlying material remains uncured. An advantage of the dual cure catalysts is that they photobleach. The activated catalyst has a significantly different absorption spectrum than the unactivated catalyst, and will transmit the light required to activate catalyst deeper in the film. This allows it to cure thick films without an inordinate increase in the light intensity or exposure time.

"One-Part" Formulations - In the unpigmented epoxy/acrylate dual cure system, as well as all pure epoxy systems, it is possible to formulate "one-part" compositions in which the uncured formulation is packaged in a single container, and does not require mixing prior to use. In comparison, most conventional epoxy resins rely on a thermal amine cure and must be packaged as two components which are mixed prior to use. Because the dual cure catalysts are photoactivated, and are inactive as catalysts before irradiation, there is less concern about incompatible materials limiting shelf life. For the urethane/acrylate system it is not possible to create a one-part composition, since the isocyanate and polyol will react at a slow rate even in the absence of a catalyst.

The disadvantages of the dual cure process as compared to other technologies include the following:

Cure Speed - Although the cure speeds of the two dual cure systems are high enough to be viable in many applications, they are slow in comparison to systems which rely on exclusively free radical cure mechanisms. Most of these are based on acrylate monomer systems, including acrylated urethane and epoxy oligomers, and have cure times as low as several seconds. In contrast, dual cure systems may require light, followed by several minutes of heat to cure completely. The use of dual cure is not the reason for these slower cure speeds. Monomers which polymerize by a cationic mechanism, such as the epoxy and urethane systems, are generally slower than those which cure by a radical process. It is this slow cationic portion of the cure process which limits the overall cure rate. The ability to get light into the system and activate the catalyst does not appear to be a problem in most cases. Rather, it is the slow thermal curing required after light exposure. The urethane containing systems are generally slower than the epoxy systems in this respect. The optimum curing sequence appears to be a short, intense light exposure, followed by a post-cure at moderate temperatures. Attempts to speed up the cure by increasing the temperature are often limited by acrylate volatility. Cure speeds may be improved by increasing catalyst levels. This may not always be possible, however, due to the discoloration introduced by catalyst residues at high concentrations. Applications in direct competition with solventless free radical based photocuring systems, where maximization of line speed is the most important variable and the physical property requirements are already being met, are not likely to be displaced by dual cure. Instead, applications should be considered which require properties superior to those possible with current technology, or which are not practical due to factors such as viscosity, pigmentation, inerting difficulties, or the undesirability of using solvents. In competition with solventborne systems, the time required for solvent evaporation prior to cure may offset slower cure speeds. Coating operations which can operate using a partial cure to a tack-free state, followed by completion of cure in an oven or after aging, may be suited to this technology. Also, applications where color is not important or can be masked so that higher catalyst levels can be used may be viable. In summary, dual cure has the best chance of success competing in applications requiring urethane or epoxy type properties in which conventional acrylate photocuring is impractical.

Residual Color - Due to the presence of iron containing catalyst residues in the cured compositions, films may exhibit a slight yellow to brown coloration. The color intensity depends on the catalyst concentration used, as well as the film thickness and transparency. Requirements for residual color vary with the particular application, and

the substrate being coated. White substrates are the most difficult. For thin, transparent films of the urethane/acrylate compositions, which generally use catalyst concentrations between 0.1 and 0.01 percent, the slight color is not a problem. In applications with stringent color requirements, the catalyst level can be decreased, with the tradeoff of longer cure time, but without affecting the physical properties. With the epoxy/acrylate systems, the problem is more severe, due to the higher level of catalyst required to cure these materials. In general, catalyst concentrations of 0.25% or higher have been found to be most effective. This limits the use of these materials to thin films (less than 1 mil), or applications where residual color is not a critical factor. In pigmented or filled systems, the residual color is often masked to a significant degree by the pigment. This allows the use of higher catalyst concentrations, and greater film thickness, without objectionable coloration.

Acrylate Monomer Exposure - The use of moderately volatile acrylate monomers in coating compositions raises the concern of worker exposure. Many of the acrylates are known to have adverse health effects. Because of this, care must be exercised when choosing an acrylate for incorporation in a formulation. The presence of acrylates in dual cure formulations will probably limit their use to industrial settings where the appropriate protective equipment and ventilation are available. The use of dual cure in the consumer market is unlikely.

Substrate Incompatibility - Because of the presence of iron compounds in the cured films, substrates which are sensitive to iron salts cannot be used. This problem is most evident when attempting to coat over PVC (polyvinyl chloride) substrates. On this substrate, iron salts are effective catalysts for the dehydrochlorination of the polymer, which causes an accelerated darkening and decomposition of the substrate, particularly under weathering conditions. For this reason, applications involving coating over vinyl substrates using the iron catalysts are effectively eliminated.

Inhibition of Cure by Fillers - During the development of dual cure primers, epoxy cure was discovered to be inhibited by a variety of pigments and fillers. The problem was traced to the adsorption and deactivation of activated catalyst on the surface of basic pigment particles. Epoxy monomers are such poor ligands for the iron cations that they are unable to compete with the more strongly complexing functional groups on the filler particles, and epoxy catalysis is shut down. This problem has not been observed in urethane system due to the stronger interaction between iron and isocyanate ligands. To overcome this

inhibition problem, surface-treatment of the filler may be necessary. Treatment with silane coupling agents was found to be an effective method of passivating the surface of silica and clay fillers for example.

Inhibition of Cure by Moisture - The inhibition of cationic epoxy cure by moisture is well known from sulfonium salt catalyzed epoxy cure systems. Cure inhibition is not dependent on catalyst, but on the chain transfer reaction between the growing epoxy polymer and water. This results in lower molecular weight and incorporation of OH functionality in the polymer. We have found similar inhibition with epoxy/acrylate dual cure formulations. Poor epoxy cure also results in reduced acrylate polymerization in dual cure systems due to increased oxygen inhibition of cure. At relative humidity levels above 50%, cure at room temperature is not practical. The only method anyone has found to improve cationic epoxy cure at high humidity is to increase the cure temperature. This has also been found to be true when dual cure catalysts are used. Often only a moderate level of heating (i.e. 50°C) is required to restore cure under humid conditions.

Application Specific Technical Assessments

Aerospace Topcoats

The development of low VOC aerospace topcoats was driven by EPA and state regulations on the aircraft manufacturing industry and airlines for a high performance protective coatings having substantially lower solvent content than currently available materials. It seemed particularly suitable as a demonstration application for dual cure because of the unusual combination of high-performance characteristics required. The combination of hardness and solvent resistance with flexibility and impact resistance seemed perfectly matched to what we had observed in for dual cure compositions in previous phases of the contract. In addition, performance requirements were well documented in military and commercial performance specifications, so we had a clear idea of the market requirements. A working relationship was established with Boeing Defense & Space Group to develop prototype topcoat formulations and evaluate their performance. Boeing provided input on their material needs and assistance in evaluation of the materials developed at 3M. A set of screening test criteria was selected from the various performance specifications. These included the properties which, in the past, were found to be the most difficult to meet simultaneously. These tests were used to direct the formulation process.

Several difficulties were encountered and resolved during the course of our topcoat development effort. Poor room temperature cure rates were improved through development of a photocatalyst/co-catalyst system which gave acceptable cure behavior. Low gloss was traced to poor acrylate surface cure and resolved through the addition of photoinitiator additives. Solvent resistance and impact resistance tradeoffs were balanced through the identification of the proper polyol, acrylates and urethane/acrylate ratio. Weatherability problems were solved through the choice of polyol and the addition of weathering additives. By the end of the contract, we had obtained a formulation which was substantially meeting the screening criteria established at the beginning of the development effort.

Unfortunately, nearly all of the solutions to performance shortcomings required the tradeoff of higher formulation viscosity. This resulted in the VOC level increasing from the originally anticipated 100 g/l to an actual level of 340 g/l when using conventional HVLP spray application equipment. We anticipate further development will allow reduction of solvent content to approximately 300 g/l. Although this is lower than the 420 g/l level obtained by the best of the conventional high solids solventborne topcoats, it may not offer enough of an advantage by itself to justify conversion to dual cure.

An additional feature offered by dual cure, which may be as attractive as solvent reduction, is increased cure speed. In conventional 2-part urethanes, the cure catalyst is active immediately upon mixing of the two reactive components. To achieve a workable potlife, cure rates must be kept low. Unfortunately, long cure times in the pot also mean long cure times on the airplane. To get a 4 hour potlife, current materials require dry times of 6 to 8 hours even when the hanger is heated to 120°F to accelerate cure. Times are longer still at ambient temperatures. With photoactivated systems such as dual cure, this tradeoff between potlife and cure time does not exist. Since the catalyst is not activated until after it has been applied, catalyst levels can be formulated for fast cure. The unactivated catalyst has no effect on cure rates in the pot, and the urethane precursors behave as if they were uncatalyzed and cure only very slowly. Potlife is improved over current materials, while cure times are decreased. The final dual cure formulation has achieved cure times of one hour. A coating is considered cured when it is "dry to tape", and can be masked for application of the next color without marring the surface. Feedback from potential users indicates that this is a major advantage. There are considerable cost savings realized when the paint cycle time is

reduced. This feature may be as important to the user as the decreased solvent level.

The feasibility of curing an object as large as an aircraft in a reasonable length of time depends to a large degree on the amount of light exposure required for cure. Long light exposure times require a larger array of lamps to cure large areas at a time. Thus it makes economic sense to minimize cure times as much as possible. This would allow use of a smaller, less expensive light source that could move along the aircraft, curing as it went.

We have found cure rates of urethane/acrylate formulations to be dependent on two factors. The first is light intensity. Sufficient light must be delivered to the coating to activate the catalysts. Higher lamp intensity means that this light dose can be delivered in a shorter time. The second factor is the urethane cure rate. Assuming catalyst activation, this depends primarily on temperature. Acrylate cure occurs only after urethane cure has begun, due to oxygen inhibition, and the overall cure rate is determined by the urethane cure rate. Depending on cure conditions, one or the other of these factors may limit the overall cure rate. At low temperatures, increased lamp intensity has little effect. As the temperature is increased, the catalyst activation rate may begin to dominate, and increased lamp intensity is beneficial. We have found that increasing both the lamp intensity and cure temperature has the largest effect on cure time. At 50° C, using Super Diazo Blue Bulbs at 2 inch spacing, cure times have been reduced to 4 minutes. This gives a cured coating which may be taped immediately after removal from the lights. This compares to a dry to tape time of several hours at 20° C with the same lights. Lowering the intensity of the lights at 50° C results in surface cure or "skinning" at short cure times due to insufficient light penetration through the pigmented film. Measurements of VOC emission levels have shown little difference in acrylate monomer loss over this temperature range. Currently, the best application procedure involves a 30 minute solvent flash time after spraying, followed by 4 minutes of light exposure at 50° C. Heating requirements will probably be met best with a radiant heat source such as IR lamps due to their faster response time. One could envision a band of lights and heaters traveling the length of the airplane after completion of spraying, curing the paint as they went. Further work to assess the feasibility of dual cure aerospace coatings and their possible advantages is in progress with the collaboration of Boeing personnel.

Aerospace Primers

The original Phase III proposal included the development of a chromated aerospace primer based on epoxy/acrylate dual cure chemistry. The primer was to be a solventless equivalent of the current 2-part epoxy primers. Like the dual cure topcoat, it would be photocured. The primer was to be optimized for use with the topcoat and provided to the customer as a unit. In part, this was driven by the perception that customers would be reluctant to use a primer made by a different supplier than the topcoat. Several technical developments and market reassessments led us to conclude that this approach might not be viable.

From the start of Phase III, there was perceived to be less of a market demand for a high solids primer. Existing regulations were being met by water reducible primers on the market at solvent levels of 350 grams per liter. Although these materials were more difficult to apply properly than earlier solvent based systems, they had become accepted by the users, and were qualified to all of the performance specifications. The industry appeared to be in the process of converting to their use. There was also the perception that chromates would be phased out of primer applications in the near future due to health and toxicity concerns. A great deal of work to find chromate replacements was ongoing, and when a substitute was found there would be a strong push for elimination of chromates. Due to the long lead time for testing, qualification and field testing of primers, it was thought that by the time a chromate-containing product reached the market it might not be usable.

Technical developments also influenced our decision. The sensitivity of cationic epoxy cure to poisoning included cure inhibition by chromates. Barium chromate worked better than strontium chromate due to its lower solubility, but both inhibited cure more than was desired. Cure was also inhibited to various degrees by other fillers. Many of these could be used only after surface-treatment. The high filler content which we found was necessary to get optimum primer performance was also leading to other undesirable effects. We realized that we were probably going to have to incorporate some solvent into our formulation to make it sprayable when fillers were present. This lessened its competitive attractiveness compared to existing materials. We were also experiencing difficulties in obtaining the properties in filled formulations that we had obtained in clearcoat formulations. This may have been due to the effect of the fillers on the degree of epoxy cure. Impact resistance in particular was greatly degraded upon addition of fillers. Humidity inhibition of cure was also found to be a problem with no apparent solution other than heating.

This was an added complication that we had not foreseen. For these reasons it was decided to suspend development of the primer and concentrate efforts on topcoat development. Topcoat testing would be done on substrates primed with the existing water reducible primers.

Electrical Tape Backing Applications

The electrical tape application has been quite successful in meeting its performance and processing goals. Dual cure catalysts were used to cure an epoxy saturant for the tape backing. This process allowed replacement of the current solvent based 2-part epoxy with a solventless, one part photocured epoxy. The new material met all of the mechanical and electrical performance criteria which had been established by the existing product. The raw materials were somewhat higher in cost, but this was overshadowed by the processing improvements made possible by dual cure. The new process operates without solvent emissions. Line speed is increased, and production can be completed in a fraction of the time required under the existing process. Energy input for operation of the solvent drying/curing oven is eliminated. The energy and expense of operating the catalytic oxidizer used for burning solvent emissions in the old process is not necessary in the new process, since no solvents are used. As the calculations in the energy analysis which follows shows, total energy consumption is two orders of magnitude lower than the existing process. Overall, the cost of production has been reduced dramatically using dual cure.

Sub-task 4.2: Economic and Cost Analysis

Generic Clearcoat Applications

The projected manufacturing costs for a generic clearcoat protective film product using the 3M Dual-Cure process were based on the information presented in the Phase II final report, as well as process data collected during coating studies in Task 3 in Phase III. Generic information derived from other coating experiments performed outside the contract was also drawn upon. Both urethane/acrylate and epoxy/acrylate formulations were considered for this application. Material costs are calculated based on a normalized cured film thickness of 1 mil, although the film thickness in actual applications will vary. The pilot-scale coating experiments in Phase II produced film thicknesses of 0.4 mil for the epoxy/acrylate

system, and 1 mil for the urethane/acrylate system. Processing costs were estimated at a scale likely to be used commercially. Monomer costs were based on quotations from the supplier based upon bulk purchases. Catalyst costs were based on estimates of the production cost at the pilot plant level.

I. Generic Protective Clearcoat Application Material Costs

A. Coating Thickness - 1 mil

B. Coating Width - 36 inches

C. Urethane / Acrylate Raw Materials:

Selected polyol	\$2.35/lb.
Selected isocyanate	\$4.20/lb.
Selected monoacrylate	\$2.47/lb.
Selected polyacrylate	\$2.17/lb.
Photocatalyst system	\$50.00/lb.

Epoxy / Acrylate Raw Materials:

Selected epoxy	\$3.89/lb.
Selected monoacrylate	\$4.16/lb.
Selected polyacrylate	\$2.82/lb.
Photocatalyst system	\$75.00/lb.

D. One square yard, coated at a thickness of 1 mil, gives a coating weight of 23 grams.

E. Formulation cost per square yard:

Urethane / Acrylate Monomers	\$0.1405
Photocatalyst system	\$0.0025
Urethane / Acrylate Total	<hr/> \$0.143
Epoxy / Acrylate Monomers	\$0.2105
Photocatalyst system	\$0.0101
Epoxy / Acrylate Total	<hr/> \$0.221

II. Protective Clearcoat Application Processing Costs

A. U.V. Cure operation - 29 kW (2 X 48" lamps @ 300 W/in.)

B. Space oven operation - \$64 / hr.

**C. Web Speed - epoxy / acrylate: 2000 yd./hr.
 urethane / acrylate: 1000 yd./hr.**

D. Totals including Equipment, Maintenance, Overhead:

Epoxy / acrylate - \$0.19 / yd.

Urethane / acrylate - \$0.37 / yd.

III. Protective Clearcoat Application Total Costs

**Urethane / Acrylate Materials - \$0.143
Processing - \$0.37**

Urethane / Acrylate Total - \$0.51 / yd.

**Epoxy / Acrylate Materials - \$0.221
Processing - \$0.19**

Epoxy / Acrylate Total - \$0.41 / yd.

Based on our experience over the course of dual cure process development, the ideal cure sequence for clearcoat applications appears to be a short, high intensity U.V. exposure, followed by a long, moderately heated (or gradient heated) oven to minimize acrylate monomer loss during the thermal cure stage. The infrared heat output of the U.V. lamps must also be controlled to avoid volatilization of the acrylate monomers. Overall costs are still quite competitive with other solvent and radiation curable systems. The major factor influencing the relative costs of the epoxy/acrylate and urethane/acrylate systems is the slower cure speed of the latter. The increased processing costs which result negate any raw material cost advantage.

Comparative Examples of Other Processes

In addition to the examples presented in the Phase I report, the following cost calculations are provided as comparative examples utilizing existing photocuring technology. When an example coating is performed at thicknesses other than 1 mil, dual cure costs have been normalized by recalculating the appropriate material costs and retaining the processing costs at a fixed level. The first is a photocurable epoxy clearcoat formulation using a triarylsulfonium salt catalyst. The formulation comes from the product information sheet for the catalyst, and it is described as a typical coating for tin plated steel can stock. The epoxy monomers used in this formulation are similar to those used in the epoxy/acrylate dual cure formulations.

- A. Raw Material Costs: Epoxy monomer blend - \$3.20 /lb.
 Catalyst - \$30.00 /lb.
- B. Coating Thickness: approximately 0.15 mil (2.6 mg/sq.in.)
- C. Raw Material Cost per Square Yard: \$0.044
- D. Line Speed: 2000 yards / hour at coated thickness. Speed would decrease for thicker coatings.
- E. U.V. Cure Operation: 20 kW (2 X 48 in. lamps @ 200 watts/in.)
- F. Total Processing Costs: \$0.183 / sq.yd.
- G. Total Costs: \$0.227 /sq.yd.
- H. Epoxy / Acrylate Cost Normalized to 0.15 mil: \$0.224 / sq.yd.

The dual cure manufacturing costs are seen to be approximately the same as those for the conventional photocured clearcoat. If film thickness was increased, dual cure would become more economical as the light absorption efficiency of the conventional catalyst decreased.

The second comparative example is of a U.V. curable acrylated epoxy oligomer thinned with acrylate monomer. This example comes from a

monomer manufacturer's product information bulletin, and is described as a medium viscosity clear coating recommended as a coating for steel.

- A. Raw Material Costs:
 - Acrylated Epoxy - \$1.62 /lb.
 - Difunctional Acrylate - \$2.17 /lb.
 - Catalyst - \$30.00 /lb.
- B. Coating Thickness: 0.6 mils
- C. Total Raw Material Costs: \$0.073
- D. Line Speed: 2500 yd./hr.
- E. U.V. Cure Operation: 9.6 kW (1 X 48 in. @ 200 watts/in.)
- F. Nitrogen Purge: \$30/hr.
- G. Post-bake at 200 C for 5 minutes
- H. Total Processing Costs: \$0.184 / sq.yd.
- I. Total Cost: \$0.26 / sq.yd.
- J. Epoxy/Acrylate Cost Normalized to 0.6 mils: \$0.32 / sq.yd.
Urethane/Acrylate Cost Normalized to 0.6 mils: \$0.46/sq.yd.

In this example, the dual cure costs are somewhat higher, primarily due to more expensive monomers and lower line speeds.

Pigmented Aerospace Coatings Application

The material cost per given coverage for a pigmented dual cure coating is expected to be only slightly more than current solvent based technology. The added expense of the acrylate monomers is largely offset by the removal of solvents and a decrease in the urethane precursor content. Also, because more of the applied coating weight is retained in the cured film, less material is required to give the same coverage and film thickness. Material costs will be somewhat increased due to the added cost of the initiator and photocatalyst additives.

The pigmented aerospace coatings developed under this contract are designed to be spray applied using conventional HVLP spray guns. For this

reason, some solvent is required to thin the coating to sprayable viscosities. For pigmented coatings prepared on a web using non-spray application techniques, some or all of this solvent could be eliminated.

The best curing conditions for the pigmented aerospace coatings developed under the contract combine light exposure with low levels of heating. Light is provided by "Super Diazo Blue" Bulbs from Sylvania or "Super Actinic" Bulbs from Phillips. These are fluorescent bulbs intended for use in diazo blueprint machines and have most of their output in the blue, centered around 420 nanometers. We used the 5 foot long, 160 watt bulbs at a 2 inch spacing with a reflector behind each bulb. We have demonstrated cure to tape 1 hour after spraying without auxiliary heat sources. This time includes a 30 minute solvent evaporation interval, followed by a 15 minute light exposure. Additional experiments showed that the light exposure time could be reduced to 4 minutes if the temperature of the substrate was increased to 50° C during light exposure. The cure rate at lower temperatures seems to be limited by the polymerization rate of the urethane rather than by the activation rate of the photocatalyst. Experiments have shown that this moderate temperature increase does not result in any detectable increase in VOC emissions due to acrylate monomer loss. Shortened exposure time simplifies the design and size of the lamp bank needed in actual use. We envision using low power infrared heaters to provide the surface heating necessary to accelerate cure. The following calculations are for the operating costs of curing pigmented aerospace coatings using supplementary heating.

Pigmented Coatings Processing Costs:

- A. Solvent evaporation time - less than 1/2 hour
- B. Light exposure time - 4 minutes @ 50° C
- C. Dry to tape time - 1 hour after spraying
- D. Electrical input to lamps - 1800 watts / square yard
- E. Lamp cure energy - 0.115 kW-hr. / sq.yd.
- F. Infrared heater electrical input - 5400 watts / sq.yd.
- G. Heater cure energy - 0.36 kW-hr. / sq.yd.

H. Total cure energy - 0.48 kW-hr. / sq.yd.

The capital costs for dual cure coating operations will be somewhat higher than for conventional 2-part urethanes due to the additional photocuring step involved. The added capital expense of the lamps and IR heaters will be offset by the greatly reduced cure time and elimination of the need to heat the paint hanger to accelerate cure. Conventional aerospace coatings require 6 to 8 hours at a temperature of 120°F to achieve dry to tape cure. Longer times are required if hanger heating is not available. This time can be reduced to 1 hour using the dual cure system. Shortened cure time provides several economic advantages. Painting facilities would be used more efficiently with shortened cycle times. The time spent waiting for the paint to dry would be eliminated. For manufacturers, shortened cycle times mean faster delivery to the customer and reduced "cost of money" expenses. Conversations with Boeing personnel have indicated that there would be savings of \$60,000 for a one day cycle time reduction on a 747 aircraft from this source alone. In addition, labor savings and reduced capital expenditure on new paint hanger construction could be realized. For airlines, reduction of out of service time for repainting operations shortens the period where the aircraft is not generating revenue. All of these savings should quickly pay for the capital expense of lamp installation.

Energy costs for operation of the curing lamps and heaters will be a minor portion of total operating expenses. The cost of electricity to power the lamps and IR heaters will be less than 5% of the cost of the coating itself, even in a worst case analysis. This small added expense will be insignificant compared to the savings gained from reduced cycle times.

Electrical Tape Backing Application

I. Raw Material Costs

- A. Dual cure resin formulation cost - \$ 3.37 / lb
- B. Dual cure resin solvent content - 0 %
- C. Existing resin formulation cost - \$ 2.08 / lb
- D. Existing resin solvent content - 30%
- E. Existing resin cost on a 100% solids basis - \$ 2.97 / lb

Raw material costs for the dual cure process are comparable to the existing process on a equal resin weight basis. Major cost savings are as a result of reduced manufacturing time due to higher line speeds, and the elimination of oven drying and the catalytic oxidizer for solvent burning. These savings are discussed in more detail in the "Energy Analysis" section below.

Sub-task 4.3: Energy Analysis

The following energy analysis includes an update of the market-wide energy analysis performed under Phase II. Also included are calculations for energy savings on an individual typical coating line, and the number of lines necessary to meet the market-wide projections. Calculations for the specific demonstration applications developed in Phase III are also presented and compared to their conventional equivalents where feasible.

The objective of the work performed under this contract was to develop a technology which will lead to a reduction in energy consumption and waste generation. Energy savings will result from the reduction or elimination of solvents from coating compositions, and the reduction in gaseous waste emissions which this will allow. Savings will occur due to the reduction in feedstock consumption and the processing energy required for solvent manufacture, as well as the energy needed to recover or destroy emissions from coating operations. This latter factor is becoming increasingly important as solvent emissions are regulated to a greater degree. Dual cure allows the replacement of many conventional solvent coating techniques by a photocuring process. The complete removal of solvent is possible in many applications, and in others, significant reductions in solvent content are possible.

In the Phase I final report, an estimate of potential energy savings was presented. As Phase II of the contract progressed, and data was obtained from further laboratory and pilot plant coating experiments, the perceived markets for this technology underwent considerable change and the energy analysis was updated. The purpose of this sub-task is to once again update the projected energy savings based on the more complete understanding of the dual cure process obtained during the development of products for actual commercial applications in Phase III.

In the Phase II energy savings analysis, the major markets considered promising for the application of dual cure included metal and wood

protective coatings, adhesives, sealants, electrical coatings and plastic coatings. Of these, the protective coatings area was perceived to be the largest market, and this remains true. In particular, photocurable pigmented coatings, cured in a batch rather than continuous manner, appeared promising. The markets in which we feel dual cure will be competitive have not changed significantly based on data obtained in Phase III. An updated analysis of each market area is included in this report.

In each market area, current and projected market volumes are given. Estimates of energy savings due to solvent elimination are made using the following assumptions. Energy content of a typical solvent (energy released on burning) is 20,000 Btu per pound. The additional energy required for solvent manufacture, distribution, and disposal is an additional 10,000 Btu per pound, for a total of 30,000 Btu per pound. Coating compositions are on average 60% solvent, unless more specific data is available. Densities are 8 pounds per gallon.

The major application areas considered promising for the application of dual cure include:

Protective Metal Coatings - The anticipated market for dual cure in the protective metal coating area is tending to favor batch coating operations rather than those done on a coating line. This reduces the importance of cure speed, which seems to be the most important performance requirement in applications such as can coating and metal coil coating. Spray is the most common application technique in this area, and low solids solventborne alkyds dominate the market, with urethanes and epoxies filling the more demanding uses. Since most of these coatings are pigmented, the ability to cure pigmented formulations, and achieve low VOC levels, is likely to generate interest in this market area, which is under considerable regulatory pressure.

Development of dual cure aerospace topcoats has shown that complete solvent elimination is not possible at the higher performance end of the market. Instead we now estimate a 50% reduction in solvent level for pigmented protective coatings. The epoxy based formulations would allow somewhat larger levels of solvent elimination than the more viscous urethane materials. Categories considered particularly promising for dual cure include machinery and equipment (36 MM gal.), high performance maintenance coatings (31 MM gal.), metal furniture and appliances (52 MM gal.), and non-automotive transportation (20 MM gal.). The transportation, machinery, and maintenance coatings in particular have very demanding

performance requirements, because they operate in rather difficult environments. The ability of dual cure to deliver increased coating toughness and solvent resistance should make it attractive. Both epoxy/acrylate and urethane/acrylate formulations can be used in these applications, depending on thermal and weathering requirements. The market volumes as of 1987 shown above were obtained from SRI International. Total volume for these markets is 139 million gallons. Assuming a 2.5% average annual growth rate, this volume should increase to 240 million gallons by 2010. This corresponds to a solvent usage of 1.15 billion pounds. A 50% reduction in solvent content would result in a savings of 575 million pounds of solvent, with an energy content of 17 trillion Btu. Assuming a 25% market share, this gives a 145 million pound reduction in solvent usage, and an energy savings of 4.3 trillion Btu.

Wood Coatings - The wood coating industry can be separated into two categories having different requirements with respect to application technique. These are flat stock coating, and the coating of three dimensional objects. Coating of flat stock is usually done on a continuous coating line of some type, and more complicated three dimensional objects, such as furniture, usually require spray application and batch drying. We feel that dual cure may perform well in both of these applications.

The three dimensional curing operations involve primarily furniture and cabinetry. For the most part, these are clear coatings. The industry is still dominated by low solids solventborne compositions, primarily nitrocellulose lacquers. Coating is primarily by spray, followed by drying in an oven. This market appears to be a good fit with the urethane/acrylate system. Urethane based formulations are used in these applications to some degree. They have very desirable properties for wood coatings, such as abrasion resistance, hardness, flexibility, and chemical resistance. Urethane drawbacks are primarily in the application and processing areas, such as price, pot life, poor solvent release, and inferior stackability (dry time between application and stacking of units). Poor solvent release and stackability mean long periods in drying ovens, which is energy intensive and increases the possibility of dust contamination. Dual cure may be able to eliminate some of the processing problems and improve physical properties. An additional desire is the ability to strip a finish from a piece of furniture if coating defects develop. This has presented a problem with the usual photocuring systems. Since they are so highly crosslinked after cure, stripping is difficult. With dual cure, it may be possible to partially cure with light, inspect the piece and strip if necessary, and then do a final thermal cure. Not having the slow solvent

removal may also reduce the number of coats which have to be applied, as well as the total time in the oven. Use with pigmented systems may also make this system more attractive to potential users. The market size for furniture and fixture coatings was reported by SRI International to be 60 million gallons in 1987, with little market growth. The U.S. market is dominated (85%) by sprayable nitrocellulose lacquers with very low solids levels of about 20%. Dual cure technology has the potential to increase the percent solids in this application to 70%. Calculations show a total market potential to eliminate 240 million pounds of solvent, with an energy content of 7.2 trillion Btu.

The second major wood coating category is flat stock. This application is about 40% solvent based, and 60% water based. The water borne coatings require an energy intensive oven bake to evaporate the water. The total market for flat stock coatings is 19 million gallons, so the solvent base portion is approximately 8 million gallons. This corresponds to 38 million pounds of solvent with an energy content of 1.1 trillion Btu.

The total solvent reduction possible in the wood coating area is approximately 280 million pounds, with an energy content of 8.3 trillion Btu. Assuming 25% market share for dual cure gives a solvent reduction of 70 million pounds and 2.1 trillion Btu.

Electrical Coatings - This market includes applications which may be suitable for dual cure, such as conformable circuit board coating, potting and encapsulation. For circuit board applications, the capability to cure in shadowed areas is important, and has slowed use of U.V. curing systems. Use of visible light, as in the dual cure system, is known to help with shadow cure. Low viscosity, to improve wetting, low cure temperature, and low cure shrinkage are also important in this application. For potting applications, the ability of dual cure to cure thick films, and pigmented films are important. Two part epoxy materials currently dominate this market, but suffer from slow cure. These two markets appear to be most suited to the epoxy/acrylate dual cure materials, although there are some urethane based conformable coatings. Electrical coatings is a low volume market. The entire electrical insulation market was reported by SRI International to be 14 million gallons per year in 1987. By the year 2010, this is projected to grow to 24 million gallons. A large proportion of this is wire coating. This corresponds to a solvent content of 115 million pounds with an energy content of 3.5 trillion Btu. Assuming a 25% market share for dual cure gives a total of 0.8 trillion Btu in energy savings.

Plastics Coatings - The coating of plastic items, either in roll form or as three dimensional objects, is an application where dual cure appears to fit well. Limitations on cure temperature due to the temperature sensitivity of the plastic substrate, and the need for good wetting by the coating, may make use of alternative solventless technologies, such as waterborne and powder coating, difficult to implement. Due to the extreme diversity in this market, volume is difficult to estimate.

Adhesives - Analysis in this report remains unchanged from Phase II. The U.S. market for adhesives in 1986 was 10.2 billion pounds, with market growth approximating GNP (Skeist Inc., Adhesives V, Oct. 1987). Of this, 476 million pounds were due to urethanes, epoxies, and acrylates. The projected total market for 2010 is 18.5 billion pounds, of which 860 million pounds is in the urethane/epoxy/acrylate category. Assuming an average of 60% solids, this gives a potential solvent savings of 350 million pounds, which corresponds to an energy savings of 10 trillion Btu. Assuming a dual cure market share of 25% leads to a projected savings of 87 million pounds of solvent and an energy savings of 2.5 trillion Btu.

Sealants - Analysis in the sealant area remains unchanged from Phase II. The total market for sealants (Skeist Inc., Sealants B, June 1987) in 1986 was 644 million pounds, with 66 million pounds due to polyurethanes, 0.5 million pounds to epoxies, and 114 million pounds to acrylics. From projected growth rates, the total market in these three areas should be 629 million pounds by 2010. Because sealant materials are likely to have a higher solids content than other coatings, we will assume a solvent content of 30% for the purpose of this calculation. Resulting solvent usage is 190 million pounds, with a potential energy content of 5.6 trillion Btu. Assuming a dual cure market share of 25% gives a solvent savings of 47 million pounds, and an energy savings of 1.4 trillion Btu. Total reduction in solvent use, and the associated reduction in energy consumption due to the energy content and manufacturing inputs associated with solvent production, is shown in Table 4.1. Total energy savings of 11.1 trillion Btu / year by the year 2010 are projected, due to an elimination of 378 million pounds of solvent per year. The uncertain contributions due to plastics coatings are not expected to increase these numbers significantly.

Table 4.1: U.S. Energy Savings Resulting from Solvent Elimination by Market Area (million pounds, trillion Btu/year)

Market	Potential		Projected	
	Solvent	Energy	Solvent	Energy
Metal	575	17.	145	4.3
Wood	280	8.3	70	2.1
Electrical	115	3.5	29	0.8
Plastics	—	—	—	—
Adhesives	350	10.0	87	2.5
Sealants	190	5.6	47	1.4
Total	1510	44.4	378	11.1

Energy savings due to process advantages are considerably more difficult to quantify. The coatings industry uses a very diverse range of application techniques and material types. One aspect of the coating process for which energy consumption estimates can be made is the energy to cure. Table 4.2 shows a variety of coating types, along with the energy required for cure.

**Table 4.2: Energy Required for Curing Various Coating Types.
(ref. 1)**

Coating Type	Energy to Cure (ref. 2)	
	(Btu/square foot)	(Thousand Btu/pound)
Water Soluble	75	14.2
High Solids Oil-free Polyester	69	13.3
Acrylic Powder Coating	45	8.6
Acid Catalyzed Lacquer	23	4.4
Hot Melt Adhesive (ref. 3)	6	1.2
U.V. Cured Pigmented	33	6.3
U.V. Cured Lacquer	4	0.8
Electron Beam Cured	8	1.5

References:

1: "American Paint Show", Polymers Paint Color Journal, vol. 170(4037), Dec. 1980, p.943.; L. Newton, "Trends and Developments in Radiation Curable Coatings", Polymers Paint Colour Journal, vol. 172(4062), Jan. 1982, p.21.

2: Gas fired ovens at 4,000,000 Btu/hr. and 70% efficiency + 15kWHr electrical. A U.V. processor requires 22 kWHr electrical (Battelle Report No. 51), V.D. McGinniss, 1987, p.22.

3: Shell Chemical Co., "Looking Ahead at PSA Economics: Analysis of Hot Melt, Emulsion, and Solvent Systems", Technical Bulletin SC4445-80, 1980.

Major inputs of energy are required when solvent evaporation is required. Two factors influence the amount of energy required at a given oven temperature. The first is the amount of solvent and its heat of vaporization. The second is the amount of air which must be passed through the oven to remove solvent vapors without exceeding the explosive limits of the solvent/air mixture. Water based coatings are

strongly influenced by the first factor, since the energy to evaporate water is roughly five times that to evaporate a typical organic solvent. Because of the lack of concern about lower explosive limit concentrations with water, the air flow rate through the oven can be reduced, which helps somewhat. High solids coating formulations attempt to reduce cure energy by reducing solvent levels to the minimum required by the application technique. Viscosity is usually the limiting factor. Solvent evaporation is rather inefficient due to its high air flow volume, which is generally between 10,000 and 50,000 cubic feet per gallon of solvent evaporated. Powder coatings are nearly 100% solids, but generally require long oven cures at relatively high temperatures. In contrast, the final three cure techniques, which involve radiation curing, have relatively low cure energies. Even with the addition of a heat post-cure, these categories would have lower energy consumption due to the use of efficient ovens requiring very little air flow.

For dual cure formulations, cure energies consist of two parts. The first of these is the U.V. exposure to activate the catalyst. Using the numbers generated in the economic analysis, Task 4.2, for light dose and line speed, we arrive at the following numbers:

I. U.V. Exposure Contribution to Cure Energy.

A. Line Speed: Epoxy / Acrylate - 2000 yd./hr.
 Urethane / Acrylate - 1000 yd./hr.

B. Electrical Consumption for Lamps : 29 kWhr. = 99000 Btu/hr.

C. U.V Cure Energy Contribution: Epoxy / Acrylate - 5.5 Btu/sq.ft.
 Urethane / Acrylate - 11 Btu/sq.ft.

For calculation of energy consumption during thermal post-cure, power requirements of an infrared oven are used as a basis for calculation. A 90 foot I.R. oven line is reported to consume 250 kilowatt hours of electricity. Since this oven operates at a higher temperature than we require, half of this number will be used. The epoxy system also requires less heat, so an oven of half this length will be used for calculation. Although this calculation is for an electrically heated oven, a gas fired oven could be used instead, with comparable energy consumption.

II. Thermal Post-cure Contribution to Cure Energy.

A. Oven Energy Requirements: 425,000 Btu/hr.

B. Oven Energy Contribution:

Epoxy / Acrylate - 11.8 Btu/sq.ft.

Urethane / Acrylate - 47 Btu/sq.ft.

III. Total Cure Energy Requirements.

Epoxy / Acrylate - 17.3 Btu/sq.ft.

Urethane / Acrylate - 58 Btu/sq.ft.

To arrive at an average cure energy requirement, it is more reasonable to calculate an average which is based on market share, rather than a simple average. This can be based on the current market volumes for urethane and epoxy coating resins, which were reported by SRI International to be 137 and 202 million pounds per year respectively in 1988. The average can cure energy can be calculated as follows:

$$[(17.3 \text{ Btu})(202) + (58 \text{ Btu})(137)] / (202 + 137) = 33.7 \text{ Btu/sq.ft.}$$

This corresponds to an energy to cure of 6.5 thousand Btu/pound. The energy savings gained by replacing various coating techniques with dual cure can then be calculated. This is shown in Table 4.3.

Table 4.3: Energy Savings for Dual Cure Replacing Other Curing Methods.

Cure Process	Process Energy - Dual Cure Energy = Savings (thousand Btu / pound)			
Solventborne	110	-	6.5	= 103.5
High Solids	20	-	6.5	= 13.5
Waterborne	14	-	6.5	= 7.5
Powder	9	-	6.5	= 2.5
Radiation Curable	4	-	6.5	= (2.5)

Energy to cure for dual cure is the market share weighted average for the urethane / acrylate and epoxy / acrylate systems.

Total cure energy savings can be calculated based on projected market shares for each of these curing techniques. Table 4.4 shows the projected volumes calculated for each of these cure methods in the year 2010 as calculated in the Phase I final report.

Table 4.4: Projected Volumes by Cure Type in 2010 and Corresponding Savings by Use of Dual Cure.

Cure Process	Volume in 2010 (million lb./year)	Potential Energy Savings (trillion Btu/year)
Solventborne	2017	209
High Solids	1879	25
Waterborne	2847	21
Powder	1270	3
Radiation Curable	254	—
Total	8467	258

Assuming dual cure is competitive in the part of the coatings market currently occupied by acrylic, urethane, epoxy, and vinyl coatings, this gives a market share of 53%. If dual cure was to be used in 10% of these markets, the following energy savings would be realized:

Total Energy Savings X Fraction Accessible X Market Share =

(258 trillion Btu) (53%) (10%) = 13.7 trillion Btu/yr.

Total Cure Energy Savings in 2010 = 13.7 trillion Btu/year

Combining the savings due to reduced cure energy requirements, with the 11.1 trillion Btu/year resulting from reduced solvent consumption gives a total projected energy savings of 24.8 trillion Btu per year by the year 2010.

Generic Dual Cure Coating - Single Coating Line Energy Analysis

Epoxy/Acrylate Urethane/Acrylate

I. Dual Cure Process

A. Market breakdown -	60%	40%
B. Web width -	36 inches	36 inches
C. Web speed -	2000 yd/hr	1000 yd/hr
D. Light energy -	3 - 36" lamps at 300 watts/inch 28 kW electric = 304,000 Btu thermal	
E. Post-cure oven energy -	100,000 Btu/hr	200,000 Btu/hr
F. Total energy usage -	404,000 Btu/hr	504,000 Btu/hr
G. Unit area energy -	202 Btu/yd	504 Btu/yd
H. Annual operation -	350 days at 2/3 efficiency	
I. Annual production -	11.26 million yd.	5.63 million yd.
J. Annual energy -	2.27 X 10E9 Btu	2.84 X 10E9 Btu
K. Annual energy / 11.26 million yd.	2.27 X 10E9 Btu	5.68 X 10E9 Btu

II. Solvent Coating Process

- A. Solvent content - 60%**
- B. Web width - 36 inches**
- C. Web Speed - 2000 yd/hr**
- D. Annual production - 11.26 million yd.**
- E. Oven energy - 4 X 10E6 Btu/hr**

F. Annual oven energy - 2.25×10^{10} Btu

G. Solvent usage - 50 grams/yd

H. Annual solvent usage - 1.24 million lbs

I. Annual solvent energy - 3.7×10^{10} Btu

J. Thermal oxidizer @ 14,000,000
Btu/hr shared by 3 lines - 3.9×10^{10} Btu / yr.

K. Total annual energy - 1×10^{11} Btu

III. Annual energy savings for 11.26 million yd. production:

Epoxy/Acrylate - 9.8×10^{10} Btu

Urethane/Acrylate - 9.4×10^{10} Btu

IV. Number of coating line equivalents needed to meet 2010 annual projected energy savings of 24.8 trillion Btu - 260

Electrical Tape Backing Saturant Energy Analysis

I. Existing Solvent-Based Process Energy Analysis

A. Cure oven temperature - 275°F

B. Cure oven energy - 800,000 Btu / hour

C. Annual oven energy consumption - 2.24×10^9 Btu / yr.

D. Thermal solvent oxidizer energy - 3.92×10^{10} Btu / yr.

E. Annual production - 1.3 million square yards (1991)

F. Solvent usage - 119000 lbs / yr. (1991)

G. Solvent energy content - 20,000 Btu / lb. solvent energy
10,000 Btu / lb. production

H. Annual solvent energy content - 3.57×10^9 Btu / yr.

I. Total annual energy usage - 4.5×10^{10} Btu / yr.

II. Dual Cure Process Energy Analysis

A. Web width - 50 inches

B. Coating speed - 150 feet / minute

C. Coating speed - 4167 square yards / hour

D. Lamps used - 3 - 50" lamps at 300 watts / inch
1 - 50" lamp at 200 watts / inch

E. Lamp power - 55 kilowatts

F. Lamp energy / square yard - 13.2 watt-hours
Thermal/electric conversion (32.4% eff.) - 45.1 Btu

G. Coater hours to meet current production - 312 hours

H. Lamp energy for annual production - 17160 kilowatt-hours
Thermal/electric conversion (32.4% eff.) - 1.8×10^8 Btu

I. Total annual cure energy - 1.8×10^8 Btu / yr.

J. Annual energy savings - 4.48×10^{10} Btu / yr.

Aerospace Topcoat Energy Analysis

I. Energy Savings Due to Solvent Reduction.

A. Aerospace 2-part urethane US market (1990)* - \$28 million

B. Aerospace 2-part urethane volume (US, 1990)* - 2.1 million lbs cured weight per year

C. Existing solvent content (approx. 50%) - 2.1 million lbs

D. Dual cure solvent content (approx. 25%) - 1.05 million lbs

E. Annual solvent reduction - 1.05 million lbs

F. Annual solvent energy savings (30,000 Btu/lb) - 45 billion Btu / year

*Reference: A.R. Marrion, A.B. Port, "New Chemistry and Technology in the Development of Isocyanate-free Paint Systems", High Value Polymers, The Royal Society of Chemistry, Thomas Graham House, Cambridge.

II. Cure Energy

A. Cure energy input - 0.48 kW-hr / sq. yd.
- 1600 Btu / sq. yd.

B. Dry weight per yard at 2 mils - 0.12 lbs

C. Annual applied area (2.1 million lbs) - 17.5 million sq. yds.

D. Annual cure energy - 28 billion Btu / year

III. Net Energy Savings - 17 billion Btu / year

The major source of energy savings, solvent reduction, is mostly offset by increases in cure energy. This analysis assumes that conventional coatings are cured at ambient temperatures and that cure is not accelerated by the application of heat. Energy inputs for heat accelerated cures would almost certainly exceed those for dual cure. The main advantage provided by the dual cure process in the aerospace market is VOC reduction and economic savings, while the energy savings appear to be modest.

TASK 5: REPORTS, CONTRACT ADMINISTRATION, AND TECHNOLOGY TRANSFER

A DoE goal throughout the contract was widespread exposure of the potential for the dual cure technology to provide substantial savings in energy usage and solvent consumption. This was accomplished via monthly reports to DoE, participation in external meetings and workshops, and presentations at various DoE sponsored meetings. During the duration of the contract, presentations on dual cure technology were made to the U.S. Air Force, via a Maintenance Technology Transfer Workshop at 3M and a 3M presentation at the Wright Laboratories Material Directorate in Dayton, OH. Several presentations on the technology were also made to Boeing Commercial and Boeing Defense and Space Group in Seattle, WA. A list of other papers published and presentations made under the contract, including Phases I and II, is shown below.

H.B. Cransford, W.M. Buck, and W.L. Chambers, "Partnership in Waste Reduction", AIChE 1990 Summer National Meeting, San Diego, CA, Paper No. 49c, August 19-22, 1990.

M.C. Palazzotto, et al., "Dual Cure Photocatalyst Systems", ACS 1990 National Meeting, Washington DC, High Solids Symposium, Paper No. 206, August 30, 1990.

M.C. Palazzotto, et al., "Dual Curable Compositions for High Solids Coatings", First North American Research Conference on Organic Coating Science and Technology, Hilton Head, South Carolina, December 3-7, 1990.

S.J. Keipert, "Dual Cure Photocatalyst Systems for Solventless Coating", First Annual International Workshop on Solvent Substitution, Phoenix, Arizona, December 4-9, 1990.

S.J. Keipert, et al., "Dual Cure Solventless Coating Process, Phase I Final Report", Contract No. DE-AC04-88ID12692, Report No. DOE/ID/12692-1 (DE92013677), February, 1992.

S.J. Keipert, et al., "Dual Cure Solventless Coating Process, Phase II Final Report", Contract No. DE-AC04-88ID12692, Report No. DOE/ID/12692-2 (DE93001351), October, 1992.

D.W. Osten, "Dual Cure Solventless Coating Process, Phase III Semiannual Technical Progress Report (October 1, 1991 - March 31, 1992)", Contract

No. DE-AC04-88ID12692, Report No. DOE/ID/12692-3 (DE98001352), October, 1992.

S.J. Keipert, "Low VOC Photocurable Topcoat for the Aerospace Industry", Third Annual International Workshop on Solvent Substitution, Phoenix, Arizona, December 8-11, 1992.

K.E. Kinzer and S.J. Keipert, "Low VOC Dual Cure Aerospace Topcoat", Pollution Prevention Conference on Low- and No-VOC Coating Technologies, San Diego, CA, May 25-27, 1993

S.J. Keipert, K.E. Kinzer and A.M. Brown, "Low VOC Dual-Cure Aerospace Topcoats", AIChE 1993 Summer National Meeting, Seattle, WA, Paper No. 3d, August 15-18, 1993.

K.E. Kinzer, "Dual Cure Low-VOC Coating Process, Phase III Semi-Annual Technical Progress Report (April 1, 1992 -September 30, 1992)", Contract No. DE-AC04-88ID12692, Report No. DOE/ID/12692-4 (DE94000365), October, 1993.

K.E. Kinzer, "Dual Cure Low-VOC Coating Process, Phase III Semi-Annual Technical Progress Report (October 1, 1992 -March 31, 1993)", Contract No. DE-AC04-88ID12692, Report No. DOE/ID/12692-5, November, 1993.

Appendix 1

Comparison of Urethane Topcoat Requirements

Specification	MIL-C-83286B	MIL-C-85285B	BMS 10-60H
<i>General</i>	low solids VOC 560-650 g/l	high solids VOC <420 g/l	
Toxicity	free isocyanate < 1.0%, aliphatic isocyanates only	free isocyanates < 1.0% No Pb <i>ASTM D 3432 & D 3335</i>	material shall be health safe curing mixing, application, and cure.
Volatile Content	min % solids from 35 to 52% depending on color <i>FTMS 141 no. 4041.1</i> <i>ASTM D 126</i>	Type I < 420 g/l Type II < 350 g/l no halogenated solvents <i>ASTM D 3960</i>	± 2% on non-volatile content <i>ASTM D 2369 & D 1353</i>
<i>Component Properties</i>			
Condition in Container	homogeneous, free from lumps, thickening, or gelatinization <i>FTMS 141 no. 3011.1</i>	homogeneous, free from lumps, thickening, or gelatinization	no caking, free from skins, livering, gelled particles when viewed on glass plate <i>FED-STD 141 no. 3011.1</i>
Storage Stability	stable for 1 year	stable for 1 year	stable for 1 year
Moisture Content	<1.75% <i>FTMS 141 no. 4081</i>	<1% <i>ASTM D 1364</i>	
<i>Liquid Properties</i>			
Fineness of Grind	gloss min. 7, camouflage min 5 on Hegman scale 1 hr after mixing <i>FTMS 141 no. 4411.1</i>	gloss min. 7, camouflage min 5 on Hegman scale 1 hr after mixing <i>ASTM D 1210</i>	
Coarse Particles		<0.5% by wt retained on no. 325 sieve <i>ASTM D 185</i>	
Odor	not obnoxious <i>FTMS 141 no. 4401</i>	no residual odor after 48 hrs, wet or dry coating not obnoxious	

Appendix 1 (Continued)

Viscosity	17 to 23 sec through no. 2 Zahn cup, with exceptions and aged 6 hr test <i>ASTM D 562</i>	<30 sec through no. 4 Ford cup at maximum VOC content <i>ASTM D 1200</i>	± 20% of value provided by the supplier
Pot Life	6 hrs, up to 20% thinner may be added, viscosity increase < 6 sec	viscosity <60 sec through no. 4 Ford cup after 4 hrs in closed container, no gel in 8 hrs <i>ASTM D 1200</i>	meet all specs at 4 hr (white), 3 hrs (other colors), or 1 hr (metallics) after mixing
Weight per Gallon			± 0.25 lb from label <i>ASTM D 1475</i>
<i>Film Properties</i>			
Drying Time	dry to recoat in 1 hr. set to touch in 2 hrs. dry-hard in 7 hrs. <i>FTMS 141 no. 4061.1</i>	set to touch in 3 hrs. dry-hard in 8 hrs. <i>ASTM D 1640</i>	
Surface Appearance	smooth, uniform, free from bubbles, pinholes, holidays, or other irregularities	uniform, smooth surface when sprayed initially or 4 hrs after mixing	good spraying properties at 8 to 10 inches <i>FED STD 141 no. 4331.1</i>
Color	match FED-STD-595 color chip after 24 hrs drying time	match FED-STD-595 color chip after 24 hrs drying time	match applicable Boeing or FED-STD 595 color standard
Infrared Reflectance		specified for aircraft grey only	
Gloss	at 60° incidence: gloss colors min 90, camouflage max 7 <i>FTMS 141 no. 6101</i>	at 60° incidence: gloss colors min 90; semi-gloss min 15, max 45; camouflage max 3 <i>ASTM D 523</i>	at 60° incidence: initial - gloss min 90; semi-gloss 20-40; flat max 5; at pot life - gloss min 87; semi-gloss 20-40; flat max 5
Hiding Power	contrast ratio min 0.85 to 0.95 depending on color <i>ASTM D 1738</i>	contrast ratio min 0.9 <i>ASTM D 2805</i>	at 2.4 mil thickness - contrast ratio 0.95 light colors, 1.00 dark colors
Pencil Hardness			HB min, some require 2B min

Appendix 1 (Continued)

Adhesion	wet tape test <i>FTMS 141 no. 6301.1</i>	after water immersion, will not peel in tape test, scrap test w/3 kg weight <i>FED STD-141 no. 6301</i> <i>ASTM D 2197</i>	
Flexibility - Impact	impact flexibility after 24" drop of test mandrel	min impact elongation Type I 40%, Type II 10%	no cracking, flaking, or loss of adhesion when forward or reverse impact of 40 in. lbs.
Flexibility - Cold Bending	-65°F, gloss 1" mandrel, camouflage 2" mandrel <i>FTMS 141 no. 6222 & 6226</i>	-60°F, Type I gloss/semi- gloss 1" mandrel, camouflage 2" mandrel, Type II no test	-65°F, 4" mandrel test after 24 cycles of 160°F (25 min) and -65°F (5 min), Type I or II.
Resistance Properties			
Fluid Resistance	allowed 1 (2 for Skydrol) pencil hardness decrease <i>FTMS 141 no. 6011</i>		no blistering, softening, cracking, or peeling after exposure @ 75°C
	24 hrs in lub oil @ 121°C	24 hrs in MIL-L-23699 lub oil at 121°C	14 days in MIL-L-7808 oil
	7 days in MIL-H-5606 hydraulic fluid @ 25°C	24 hrs in MIL-H-83282 hydraulic fluid at 66°C	14 days in MIL-H-5606 hydraulic fluid
	7 days in Skydrol 500B @ 25°C		30 days in BMS 3-11 hydraulic fluid, min pencil hardness of B on dry film
	4 days in distilled water @ 100°F		7 days in distilled water, no blisters larger than #8 per <i>ASTM D 714</i>
	7 days in TT-S-735 Type III fluid @ 25°C		14 days in TT-S-735 Type III fluid

Appendix 1 (Continued)

Weather Resistance	500 hrs carbon arc 1 yr outdoor in FL, 10% loss in gloss permitted <i>FTMS 141 no. 6152</i>	500 hrs Xe weatherometer 1 yr Key West, FL, gloss at 60° gloss min 80, semi-gloss min 15, camouflage max 3	gloss retention > 70 after 500 hrs artificial weathering, >60 after 300 hrs in Atlas UVCON weathering device; free film tensile of 2000-6000 psi and min 50% elongation after 2000 hrs artificial weathering
Humidity Resistance	30 days @ 95% RH & 120°F <i>FTMS 141 no. 6201</i>	30 days @ 100% RH & 120°F <i>ASTM D 2247</i>	
Heat Resistance	4 hrs @ 300°F <i>FTMS 141 no. 6051</i>	1 hr @ 250°F <i>FED STD-141 no. 6051</i>	
Solvent Resistance		rub with MEK soaked rag	
Tape Resistance	no marring by masking tape after 6, 7, or 16 hrs depending on color	no marring by masking tape after 8 hrs of air dry	no staining & only slight visible mark after 6 hrs of drying in oven at 90°F
Salt Spray Resistance	500 hrs in 5% salt spray with no visible corrosion <i>FTMS 141 no. 6061</i> <i>ASTM B 117</i>		no corrosion extending > 1/8 in beyond scribe mark after 3000 hrs exposure to salt spray fog
Electrical Resistance			0.07 megohm min.
<i>Working Properties</i>			
Cleanability		90% min cleaning efficiency	
Strippability		90% stripped in 60 min with MIL-R-81294 paint remover	

Appendix 2

Comparison of Epoxy Primer Requirements

Specification	MIL-P-23377F	MIL-P-85582A	BMS 10-79K
<i>General</i>	Class 1 - Standard Solvents Class 2 - High Solids Class 3 - Exempt Solvents	Epoxy, Waterborne bisphenol-A-type Epoxy Cl 1 - Ba chromate Cl 2 - Sr chromate	Corrosion Resistant Primer Gr A - Conventional Solvents Gr B - Low VOC/Exempt Solvent Gr C - Low VOC/Conv. Solvent Type II Urethane compatible Type III <1% aromatic amine
Toxicity	No lead permitted <i>ASTM D 3335</i>		
Chromate Content (in component A)	Type I min 52% of pigment weight, Type II min 42%, must be strontium chromate.	Type I & II: CrO ₃ min 15.7% of pigment weight Type I TiO ₂ min 13.0%	
Pigment Content	Component A contains min % solids: Cl 1 & 2 - 37%, Cl 3 - 35%	min 45% of solids in admixed primer <i>FTMS 141 no. 4021</i>	
Volatile Content	Cl 2 & 3 <340 g/L <i>ASTM D 3960</i>	<340 g/L; chlorinated solvents not permitted	Gr A: apx 650 g/L Gr B & C: < 350 g/L
<i>Component Properties</i>			
Condition in Container	homogeneous, free from lumps, thickening, or gelatinization <i>FTMS 141 no. 3011.1</i>	homogeneous, free from lumps, thickening, or gelatinization <i>FTMS 141 no. 3011.1</i>	homogeneous, free from lumps, thickening, or gelatinization <i>FTMS 141 no. 3011.1</i>
Thinner	Cl 1 & 2 - compatible with any MIL-T-81772, type II thinner, Cl 3 - compatible with 1,1,1-trichloroethane	water, must meet type IV requirements of ASTM D 1193	

Appendix 2 (Continued)

Fineness of Grind	min 5 on Hegman scale <i>ASTM D 1210</i>	min 5 on Hegman scale <i>ASTM D 1210</i>	min 5 on Hegman scale <i>ASTM D 1210</i>
<i>Liquid Properties</i>			
Storage Stability	stable for 1 year <i>FTMS 141 no. 3022</i>		Grade A 12 mo, Gr B 9 mo, Gr C 6 mo.
Accelerated Storage Stability	stable for 7 days @ 60°C <i>FTMS 141 no. 3019</i>	stable for 7 days @ 49°C <i>FTMS 141 no. 3019</i>	
Freeze thaw Stability		meet all requirements after 5 freeze thaw cycles <i>ASTM D 2243</i>	
Color	Type I - deep yellow Type II - dark green	Type I - light green Type II - dark green	
Odor	not obnoxious <i>ASTM D 1296</i>	not obnoxious <i>ASTM D 1296</i>	no discomfort to operator
Viscosity	CI 1 & 3: 22 sec through no. 4 Ford cup; CI 2: 40 sec through no. 4 Ford cup <i>ASTM D 1200</i>	solids > 20% when thinned to 14 sec through no. 4 Ford cup <i>ASTM D 1200</i>	Grade A: 35 ± 5 sec no. 1 Zahn cup, Grade B: 12-16 sec no. 2 Zahn cup, Grade C: 3500-9500 cps @ 20 rpm no. 4 spindle in Brookfield Viscometer
Pot Life	CI 1 & 3 <30 sec through no. 4 Ford cup after 8 hrs; CI 2 < 70 sec through no. 4 Ford cup after 4 hrs	when initially thinned to 14 sec & constantly stirred @ 140 rpm, < 22 sec through no. 4 Ford cup after 4 hrs	Grade A: 8 hrs, Gr B 6 hrs, Gr C 3 hrs
Total Solids	admixed primer CI 1 - 42%, CI 2 - 65%, CI 3 - 38% min by weight <i>ASTM D 2369</i>	admixed primer 40% min by weight <i>ASTM D 2369</i>	
<i>Film Properties</i>			
Drying Time	CI 1 & 3: tack-free in 1 hr, dry-hard in 6 hrs. CI 2: tack-free in 5 hrs, dry- hard in 8 hrs <i>ASTM D 1640</i>	tack-free in 1 hr, dry-hard in 6 hrs. <i>ASTM D 1640</i>	dust free 30 min, tape masking 2 hrs, overcoating w/o loss of adhesion 2 hrs.

Appendix 2 (Continued)

60° Gloss		Primer only, max 10 units @ 24 hrs, Primer & Topcoat, min 90 <i>ASTM D 523</i>	
Surface Appearance	no sagging, running or streaking, free from grit, seeds, craters, blisters, or other irregularities	no sagging, running or streaking, free from grit, seeds, craters, blisters, or other irregularities	
Infrared Reflectance	Type II only <10% in range 450 to 2700 nm	Type II only <10% in range 450 to 2700 nm	
Lifting	no evidence of lifting upon applying a polyurethane topcoat after 5 hr air dry	no evidence of lifting upon applying a polyurethane topcoat after 2, 4, & 18 hr air dry	
Solvent Retention	CI 3: retain <1% of original solvent @ 7 day, room temp. cure <i>ASTM F 151</i>		
Strippability	90% removal in 60 min @ room temp with MIL-R- 81294, type I, CI 1 paint remover	90% removal in 15 min @ room temp with MIL-R- 81294 paint remover	
Dry Adhesion		Parallel groove adhesion of not less than 4 microknife adhesion units <i>ASTM D 2197 Method B</i>	No removal with dry tape peel
Wet Adhesion	24 hr immersion in water <i>FTMS 141 no. 6301.1</i>	24 hr immersion in water <i>FTMS 141 no. 6301.1</i>	7 day immersion in water, no removal with tape peel
Flexibility - Impact	min impact elongation 10%	min impact elongation 10%	Grades A & B only: no cracking @ 40 in-lbs.
Flexibility - Bending			Grades A & B only: 180° conical bend <i>ASTM D 522</i>

Appendix 2 (Continued)

Flexibility - Low Temperature Shock			24 cycles: 160 to -65°F, 4 in mandrel bend at -65°F
Pencil Hardness			min H BSS 7263
Compatibility with Epoxy Primers			shall adhere to BMS 10-11 type I and BMS 10-20 type II
Compatibility with Urethane Topcoats			All BMS 10-60 type II materials meet adhesion, hydraulic fluid resistance, and corrosion tests
<i>Resistance Properties</i>			
Fluid Resistance	when topcoated, 4 days in distilled water @ 120°F	when topcoated, 4 days in distilled water @ 120°F	
	24 hrs in lub oil @ 121°C	24 hrs in lub oil @ 121°C	
	24 hrs in MIL-H-83282 hydraulic fluid @ 66°C	24 hrs in MIL-H-83282 hydraulic fluid @ 66°C	30 days in BMS 3-11, Grades A&C no softer than HB, Gr B no softer than 4B
Solvent Resistance	rub with 1 d rag back and mes	rub with MEK soaked rag back and forth 25 times	
Rain Erosion Resistance			primer and topcoated system peels less than 1/4 inch during 30 min test
Salt Spray Resistance	1000 hrs in 5% salt spray with no visible corrosion on Al, 500 hrs on graphite/epoxy FTMS 141 no. 6061 ASTM B 117	1000 hrs in 5% salt spray with no visible corrosion on Al, 500 hrs on graphite/epoxy FTMS 141 no. 6061 ASTM B 117	Type II primer, 500 hrs Type II primer + topcoat or Type III primer, 3000 hrs 5% salt spray
Filiform Test	1 hr in desiccator with 12N HCl, 1000 hrs @ 104°F and 80% humidity, panel primed and topcoated ASTM D 2803	1 hr in desiccator with 12N HCl, 1000 hrs @ 104°F and 80% humidity, panel primed and topcoated ASTM D 2803	1 hr in desiccator with 12N HCl, 30 days @ 104°F and 80% humidity, panel primed and topcoated

Appendix 2 (Continued)

Electrical Resistance			0.06 Mohm-cms min
<i>Working Properties</i>			
Mixing	blend to smooth homogeneous product	blend to smooth homogeneous product	
Dilution	no incompatibility with thinner, does not separate into visually distinct layer after standing 1 hr.	no incompatibility with thinner, does not separate into visually distinct layer after standing 1 hr.	
Application	smooth uniform film with no runs or sags at 0.6 to 0.9 mil dry thickness		smooth uniform film with no runs or sags at 0.6 to 0.9 mil dry thickness

DATE

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