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F & F, Research Division

Experimental Station Laboratory

Research Report

POLYURETHANE MODIFIED ACRYLIC ENAMELS

1. Acrylic Prepolymers/Polyisocyanates
2. Pot-Life Extenders/Catalysts
3. Desmodur N Modified Acrylic Clears

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INTRODUCTION

Aliphatic isocyanate based finishes have increased their market penetration considerably since their introduction several years ago despite their high cost compared to conventional finishes. Their outstanding features comprise excellent durability, color retention, and chemical resistance which other systems including finishes based on aromatic isocyanates cannot match. For this reason, the aliphatic isocyanate finishes, in particular systems based on Desmodur N/Desmophen 650, are now being used almost exclusively for painting jet aircraft. They have also made inroads in the railway industry, in construction, and other special applications.

Successful completion of this project should result in a new line of polyurethane modified acrylic finishes for aircraft, railway, and automotive applications enhancing our ability to meet future competition. We think that these finishes will be superior to Desmodur N/Desmophen 650 based coating systems in durability, flexibility, and color retention at lower cost.

OBJECTIVES

The overall objective is to develop profitable, nondiscoloring, durable polyurethane modified acrylic enamels for industrial and automotive end uses.

The immediate technical objectives are to determine if the selected 70 MMA/30 HEA-Desmodur N system meets the requirements for aircraft, railway, and automotive refinish applications and to assist Marshall Development Laboratory in further development of this or modified candidates for commercialization.

SUMMARY AND CONCLUSIONS

The emphasis of our work during the reporting period was on the development and evaluation of two-package white and clear Desmodur N modified acrylics.

Particular attention was given to the development of the acrylic prepolymers including 70 MMA/30 HEMA, 70 MMA/30 HEA, and 70 EA/30 HEA. All three prepolymer combinations were scaled-up successfully using Marshall Lab's 20-gallon kettle. Special polymerization procedures were worked out to assure the production of

clear, colorless polymer solutions of high conversion. The preferred solvents for the 70 MMA/30 HEMA and 70 MMA/30 HEA polymers are mixtures of n-butyl acetate and Cellosolve acetate. The most efficient catalyst is t-butyl peroctoate for the polymerization conditions chosen. The 70 MMA/30 HEA prepolymer was chosen for further evaluation and development because of its better overall properties including flexibility and initial gloss compared to the 70 MMA/30 HEMA composition. The 70 MMA/30 HEMA as well as a previously scaled-up 70 EA/30 HEMA copolymer were formulated into paints by Marshall Lab personnel and used to refinish passenger cars. Field testing of the 70 MMA/30 HEA paints has also been initiated.

The 70 EA/30 HEA-Desmodur N system will also be evaluated as topcoat for Corfam® poromeric material at Old Hickory.

The search for a better and less expensive pot-life extender than acetyl acetone has been unsuccessful so far. However, the use of triethylenediamine (DABCO) as catalyst may eliminate the necessity for a pot-life extender. Preliminary results indicate that DABCO catalyzed coating solutions have satisfactory pot life ($>$ 8 hours) and curing rates. Hardness build-up and gloss retention (AWC-II) of DABCO cured coatings are equal or better compared to the conventionally cured DTDL-acetyl acetone systems. Yellowing does not seem to pose a problem. This lead will be explored further.

A 70 MMA/30 HEA-Desmodur N clear coating was found to be an attractive candidate for aluminum trailer and truck finishes.

Several Weather-Ometer exposure series of Desmodur N modified acrylic coatings were concluded. Overall results indicate that the gloss retention increases in the following order:
80 EA/20 HEMA $<$ 70 EA/30 HEMA $<$ 70 MMA/30 HEA/30 MMA/30 HEMA.
The differences in gloss retention between 70 MMA/30 HEA and 70 MMA/30 HEMA are insignificant. Increasing levels of humidity during curing results in somewhat poorer gloss retention while excess Desmodur N75 (up to 10%) and deficiency of Desmodur N (minus 10%) has no significant effect on gloss retention.

Florida exposure (6 months) shows a greater tendency of mildew formation on the polyurethane modified acrylics compared to Desmodur N/Desmophen 650 (Model I). We will determine the practical significance of this observation.

Evaluation including AWC-II and Florida exposure of polyurethane modified acrylic clear coatings for aluminum is in progress.

Nafton's (supplier of Desmodur N) toxicity reports indicate that Desmodur N has low toxicity. Haskell Laboratory has started testing of urethane enamels to determine their toxicity relative to other well established coating compositions.

ACTION TAKEN OR PROPOSED

The Marshall Development Laboratory will continue formulation and field testing of preferred candidates in various market areas. A special effort will also be made by the Development Laboratory to develop a new primer for the polyurethane enamels and to further evaluate the amine cure of these systems.

In the coming period, our work will concentrate on optimization of the MMA/HEA-Desmodur N system including polymer characterization, prepolymer scale-up, definition of the mildew problem, and ways to reduce cost. The search for alternatives to acetyl acetone pot-life extenders including the study of potentially useful catalyst systems will continue.

PATENT STATUS

Competitive Patents

In addition to the references given in previous reports (Refs. 1, 2), the following patents may have a bearing on our work:

U.S. 3,351,573 to Allied Chemical Corp., patented Nov. 7, 1967, claims isocyanate pending can-stable tin catalyzed coating compositions.

U.S. 3,367,956 to Bayer, A.G., patented Feb. 6, 1968, claims a process for the preparation of biuret polyisocyanates.

U.S. 3,392,183 to Bayer, A.G., patented July 9, 1968, claims a process for the preparation of biuret polyisocyanates.

Neth. 6,611,071 to Std. Products Co., patented Feb. 6, 1968, claims polyurethanes terminated with NCO and acrylate groups.

Fr. 1,532,739 to Allied Chemical Corp., patented July 30, 1968, claims polyurethane coating compositions containing prepolymers derived from 4,4'-methylene-bis-(cyclohexylisocyanate).

Neth. 6,802,858 to Ferro Corp., patented Sept. 2, 1968, claims polyurethane coating compositions catalyzed with tin compounds containing aromatic groups.

Brit. P. 1.090,449 to Allied Chemical Corp., patented Oct. 12, 1966, claims 4,4'-methylene-bis-(cyclohexylisocyanate) based coating compositions.

Du Pont Patents

FFD-3093, covering durable, nondiscoloring, chemical resistant coatings from hydroxy bearing acrylic prepolymers and aliphatic isocyanates was filed Nov. 11, 1968. This case will be refiled to include a claim for amine catalyzed compositions in which the amine is part of the acrylic prepolymer backbone.

FFD-1301, claiming urethanes and poly(methyl methacrylate) containing urethane coatings, transferred to Legal Department on Dec. 23, 1968.

Elchem's PC-3586, claiming polyurethane coating compositions using organotin catalyst/pot-life extender combinations, was filed on Nov. 12, 1968.

It is the Legal Department's opinion that United Aircraft's patent U.S. 3,314,834, patented April 18, 1967, claiming the use of acetyl acetone as a curing rate modifier in two-package polyurethane propellants does not interfere with Du Pont's patent applications PC-3586 and FFD-3093.

Elastomer Chemicals Department Patent Cases Irwin 5X and 5Y (formerly LC-1084) claiming Hylene® W were filed 5/12/67 and have issued in England as Brit. P. 1,117,629 (6/19/68) and Brit. P. 1,127,338 (9/18/68).

ACKNOWLEDGMENTS

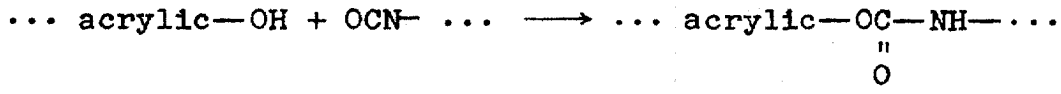
The assistance and advice of H. P. Fanning, H. B. Hitchins, W. H. Steinmetz, and G. C. Sun of the Marshall Laboratory; J. P. Herring, Engineering Department; and E. B. FitzGerald, Exp. Station, are greatly appreciated.

DISCUSSION

I. Polyurethane Modified Acrylics

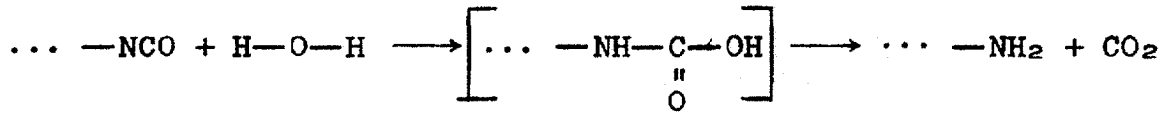
Several recent publications (Refs. 3-8) describe the progress made with isocyanate finishes in general and isocyanate modified acrylics in particular (Ref. 9).

The coatings systems developed under this project consist of hydroxy pending acrylic copolymers which are reacted with polyisocyanates to form polyurethanes.



The coating composition is a two-package system which crosslinks at room or elevated temperature and has a limited pot-life.

The moisture introduced into the coating solution by the solvents and pigments, as well as the moisture present in the air during the curing stage, can lead to the formation of polyurea as by-product.



carbamic acid
(unstable)

polyurea

The urea can further react with isocyanate to form a biuret structure. A similar reaction can also occur between the urethane and isocyanate to give an allophanate. The latter two reactions, however, are slow at room temperature, but can be a factor in baking compositions.

II. Acrylic Prepolymer

The acrylic prepolymers investigated include combinations of EA/HEMA, EA/HEA, MMA/HEMA, and MMA/HEA. The emphasis in the reporting period was on 70 MMA/30 HEMA and 70 MMA/30 HEA. The latter composition was chosen for further evaluation because of its better flexibility and initial gloss as well as lower viscosity compared to the corresponding 70 MMA/30 HEMA system. Cost and durability of MMA/HEMA, however, is slightly preferable to MMA/HEA.

The durability (gloss retention of white coatings) of Desmodur N modified acrylics increases in the following order as observed from AWC-No. II exposures:

MMA/HEMA > MMA/HEA > EA/HEMA > EA/HEA

Hardness increases and flexibility decreases in the same order. The % OH varies with the copolymer ratio as follows:

Copol. Comp. (molar ratio)	70 EA 30 HEA	70 EA 30 HEMA	70 MMA 30 HEA	80 MMA 20 HEA	70 MMA 30 HEMA	Desmophen 650
% OH	4.87	4.68	4.87	3.22	4.68	8.0

The % OH of Desmophen 650 is considerably higher compared to the acrylic prepolymers. The OH content of the acrylics does not change much with the type of monomer used and only a change in the molar ratio of the monomers has a significant effect on the % OH. The lower OH content of the acrylics accounts for most of the lower cost of the acrylic system because less of the costly isocyanate is used as compared to the competitive Desmodur N/Desmophen 650 system (Model II). Whether additional cost advantages can be realized by changing from the presently used 70 MMA/30 HEA ratio to a 80 MMA/20 HEA ratio without sacrifice in flexibility, gloss, and chemical resistance will have to be established.

The molecular weight (weight average) of a 70 MMA/30 HEMA copolymer (Gardner-Holdt viscosity of 40% solids solution in n-butyl acetate/Cellosolve acetate was K = 2.70 Poise) was found to be 33,000. The corresponding 70 MMA/30 HEA polymerization carried out under similar conditions results in lower viscosity solutions (Gardner-Holdt viscosity of 40% solution was D/E = 1.12). Molecular weight determination of this polymer is in progress. In general, it is found that the replacement of methacrylate by acrylate results in lower viscosity polymer solutions. This may be due to branching of the acrylates during polymerization.

An increase in the OH content of the acrylic prepolymers leads to compatibility and solubility problems in some cases and, in addition, would increase the cost of the coatings system.

A. Solvents

Solvents for the acrylic prepolymers include n-butyl acetate, Cellosolve acetate, methylethyl ketone, ethyl acetate, methyl isobutyl and methyl isoamyl ketone, or mixtures thereof. Most of the MMA/HEMA and MMA/HEA polymers were prepared in a mixture of 3.5 n-butyl acetate/1 Cellosolve acetate because of their favorable reflux temperature/catalyst half-life time relationship. Lately, a small amount of ethyl acetate is added to avoid popcorn-polymer formation at the monomer feed-line inlet or in the reflux condenser. This solvent mixture also gives a good balance of gloss, leveling and rate of drying. The use of all Cellosolve acetate results in hazy coatings from the DTDL catalyzed compositions. This is probably due to crosslink formation before solvent evaporation leading to shrinkage and micro-wrinkling of the coating later. The amine cured coatings, however, do not show this phenomenon and can tolerate excess Cellosolve acetate.

With the exception of acetyl acetone, the various solvents used with a 70 MMA/30 HEMA-Desmodur N coating solution had no significant effect on the pot-life as can be seen from Table I. Diglyme extended the pot-life above seven hours, but the coating solution turned cloudy and evolved gas.

The acrylate polymers are more soluble than the methacrylate containing polymers. A 70 EA/30 HEA prepolymer is, for example, soluble in a 50/50 mixture of ethyl acetate/xylene, while the other polymer compositions can only tolerate much smaller portions of xylene or none at all.

B. Polymerization Catalysts

A variety of catalysts can be employed depending on the polymerization temperature. For practical and cost reasons, polymerization at reflux temperature and a cycle of eight hours or less is preferable. High polymerization temperatures also lower the molecular weight of the polymer effectively. The best overall polymerization procedure for 70 MMA/30 HEA and 70 MMA/30 HEMA employs 3.5-4.0% (of monomer) of t-butyl peroctoate using mixtures of n-butyl acetate/Cellosolve acetate/ethyl acetate as solvents. The scale-up polymerization procedure of a 70 MMA/30 HEA copolymerization is described in

detail in the Experimental Section. This catalyst gives clear colorless polymer solutions of low viscosity. The monomer conversion is above 98.5%. The t-butyl peroctoate has a half-life of ~ 5.5 minutes at 115°C. Tertiary butyl peracetate can also be used, but the polymerization time is longer (half life at 120°C is 2.0 hours) and the conversion was not as good under the conditions chosen.

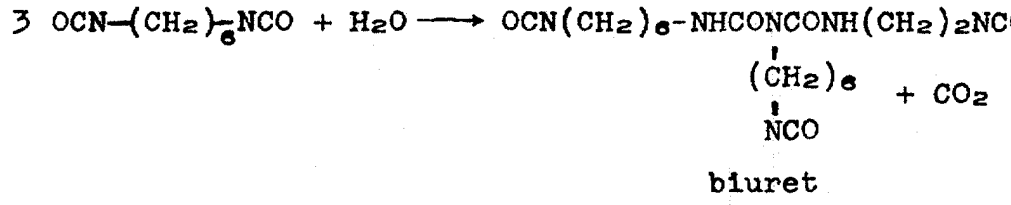
For polymerization at higher temperatures, e.g., in Cellosolve acetate at 145-155°C, di-tertiary butyl peroxide or 2,5-dimethyl-2,4-di(t-butylperoxy) hexane (Lupersol 101) can be used successfully.

Vazo® polymerization catalyst is unsuitable for the preparation of low viscosity MMA/HEMA and MMA/HEA copolymers. It also tends to discolor the polymer solutions. It, however, proved to be a useful catalyst for the preparation of a 70 EA/30 HEA copolymer in ethyl acetate/xylene at 86-89°C (see Experimental Section).

III. Polyisocyanates

Only the aliphatic or alicyclic polyisocyanates give durable nondiscoloring coatings. While some progress has been made to improve the light stability of aromatic isocyanates, such as in "Desmodur" L (Ref. 10) and Nafton's E-268 (Ref. 11), they cannot match yet the light stability of the aliphatic isocyanates. A previous report (Ref. 2) lists the various available aliphatic polyisocyanates. Of these, only "Desmodur" N was used in our work mainly because of its lower toxicity and proven acceptability in the field. Du Pont's alicyclic diisocyanate "Hylene" W has not been evaluated further because of potential toxicity hazards.

"Desmodur" N is a hexamethylene diisocyanate biuret obtained from the reaction of hexamethylene diisocyanate and water. The urea formed is reacted with additional HMDI to the biuret.



biuret

Isophorone diisocyanate, which has two NCO groups of different reactivity, may be of particular interest for systems involving isocyanate pending prepolymers.

IV. Pot-Life Extenders

Our search for pot-life extenders having similar or better effectiveness than acetyl acetone has continued.

Kojic acid, a known metal complexing agent, was found to be a very effective pot-life extender in a DTDL catalyzed 70 MMA/30 HEA-Desmodur N composition as shown in Table II-A. This effect, however, is only obtained at an unacceptable sacrifice in tack- and tape-free time of the coatings.

The addition of 2-butanol and t-butyl alcohol to a Desmodur-N modified 70 MMA/30 HEMA coating solution did not result in an extension of the pot life. We had hoped that secondary or tertiary alcohols would form a labile addition product with the isocyanate which could then be reversed by interaction with the primary OH groups of the acrylic prepolymer and lead to polyurethane formation.

The addition of citric acid, which is also a metal chelating agent, results in a cloudy, gas-evolving coating solution. The results are summarized in Table II-B.

Other efforts to extend pot-life without sacrifice in drying properties include catalyst studies which are discussed in paragraphs V-A and -B.

V. Curing of Desmodur N Modified Acrylics

The NCO-OH crosslink reaction in the absence of added catalysts is too slow for practical applications. Certain metals and aliphatic tertiary amines are the most effective catalysts for this reaction as discussed in the following paragraphs.

A. Metal Catalysis

DTDL is the best overall catalyst for curing of polyurethane modified acrylics. However, because of its high activity, combination with a pot-life extender such as acetyl acetone is necessary to keep the coating solutions from premature gelation. This system gives an acceptable balance of rate of cure and pot-life, but it necessitates separate packaging of the pot-life extender/catalyst portion because of the reaction of the acetyl acetone with the tin can. It also softens presently used primers and its enol form reacts slowly with the isocyanate. The high cost of acetyl acetone ($0.91/lb) is also an important consideration in the economics of the coating system.

Our efforts to find a better metal catalyst system were unsuccessful so far. Various metal acetyl acetonates were screened including the acetyl acetonates of vanadium, chromium, cobalt, zinc, zirconium, titanium, potassium, and nickel. The metal acetyl acetonates mentioned above are either insoluble, deeply colored, ineffective, or do not give an acceptable balance of cure rate and pot life.

We found recently that phenyl mercury propionate and phenyl mercury oleate, which are commonly used mildewcides, catalyze the NCO-OH reaction. Preliminary experiments indicate that 0.1% (rel. to coating solution solids) of these compounds result in acceptable cure rates in the absence of DTDL or DABCO. These compounds are also expected to improve the mildew resistance of polyurethane coatings.

We plan to evaluate several tin acetyl acetonates which will be prepared and supplied by Prof. S. Yolles of the University of Delaware.

B. Amine Catalysis

Tertiary amines are known to catalyze polyurethane formation. We evaluated triethylenediamine (DABCO), heptamethylisobiguanide and dimethylaminoethyl ether (NIAX-AI) as catalysts for polyurethane modified acrylics and Desmodur N/Desmophen 650 (Model II). Only DABCO gave an acceptable balance of cure rate and pot life.

In Table III, we have summarized the coating properties of a white Desmodur N/Desmophen 650 finish catalyzed with various amounts of DABCO and NIAX-AI. The results show that in this case the addition of 0.2% DABCO to the coating solution gives a gel time of more than eight hours, but the tack- and tape-free time is increased to 2, respectively six hours. The best overall balance of properties is expected to be obtained with a level of 0.25% of DABCO relative to binder. NIAX-AI, which is a good catalyst for moisture cure isocyanate systems, was found to be too slow in the above system at the levels evaluated.

Desmodur N modified acrylic coating systems require a higher DABCO level for acceptable cure rates compared to Desmodur N/Desmophen-650. A 70 MMA/30 HEMA-Desmodur N coating catalyzed with 0.5% DABCO gave a tack-free time of 1.5 hours and a tape-free time of 3 hours. The gel time was above 8 hours. Comparisons of DTDL and DABCO catalyzed coatings systems are presented in Table VI. Evaluation of amine cured MMA/HEA-Desmodur N systems is in progress.

C. Curing Under Varied Humidity Conditions

A 70 EA/30 HEMA-Desmodur N white coating composition was cured at 23, 50, and 90% relative humidity. The hardness of the coatings cured at 50 and 90% relative humidity was lower and the flexibility better compared to the coating cured at 23% rel. humidity. Tack- and tape-free time, as well as gloss of all three coatings, were essentially the same. The results are summarized in Table IV.

The gloss retention of the panels exposed on the AWC-II Weather-Ometer decreases somewhat with increasing humidity levels during cure as will be discussed in paragraph VI-B.

D. Effect of NCO/OH Ratio on Curing and Properties

A 70 MMA/30 HEA white coating solution was modified with 1.5, 5.0, and 10% excess and a 10% (by weight) lack of Desmodur N-75. The properties are summarized in Table V. While tack- and tape-free time and hardness of the coatings are similar, the impact resistance of the coating with the 10% lack of Desmodur N-75 is poorer compared to the other coatings. The gel time of all coating solutions was above 8 hours. No significant differences in gloss and gloss retention of the coatings were observed before and after AWC-II Weather-Ometer exposure.

VI. Evaluation of White Desmodur N/Acrylic Coatings

Drying characteristics and properties of white Desmodur N modified acrylic coatings have been described in a recent report (Ref. 2). In the following, up-dated results and observations are discussed.

A. Physical/Mechanical Properties

We concentrated in the reporting period on the evaluation of white Desmodur N modified 70 MMA/30 HEMA coating compositions. The results are summarized in Table VI. All paints were pigmented with W-185 because of earlier results (Ref. 2) indicating better gloss retention compared to W-131. The pigment/binder ratio was in most cases 64/100 except when stated otherwise. The coatings were sprayed on Alodine Al 1200S substrate and Alclad Al primed with 818-012 Pretreatment Coating Wash Primer and 825-8140 "Corlar" Intermediate Coat White. In order to follow the application conditions in the field, the primer was cured for a minimum of 4 hours

and a maximum of 36 hours at room temperature. Gloss, leveling, impact resistance and flexibility of the 70 MMA/30 HEMA-Desmodur N system does not quite match the competitive Desmodur N/Desmophen 650 finish yet. We have, therefore, recently shifted the emphasis to 70 MMA/30 HEA-Desmodur N systems which appear to overcome these shortcomings. Detailed evaluation is still in progress.

The addition of 1,4-butanediol to a white 70 MMA/30 HEMA-Desmodur N paint in order to increase the OH content from 4.7 to about 8%, which matches Desmophen 650, did not result in a significant improvement in gloss or impact resistance.

B. Exposure Series - Durability

The AWC-II Weather-Ometer exposure results of white Desmodur N modified 70 EA/30 HEMA, 80 EA/20 HEMA, 70 MMA/30 HEA and 70 MMA/30 HEMA coatings (Exposure Series 21608) show superior gloss retention compared to Desmodur N/Desmophen 650 except the 80 EA/20 HEMA-Desmodur N systems which were similar to Desmodur N/Desmophen 650 after 300, 600, and 900 hours. The 70 MMA/30 HEMA-Desmodur N coatings showed the best gloss retention.

AWC-II (Exposure Series 21669) exposure of white 70 EA/30 HEMA-Desmodur N coatings cured at 23, 50, and 90% relative humidity shows that gloss retention decreases with increasing humidity after 600 and 900 hours. White 70 MMA/30 HEA-Desmodur N coatings formulated with up to 10% excess as well as a 10% deficiency of Desmodur N-75 showed no significant differences in gloss retention. A 70 MMA/30 HEA-Desmodur N coating baked for 30 min. at 130°C had better gloss retention than its air-dried counterpart.

AWC-II (Exposure Series 21718) exposure of DABCO cured 70 MMA/30 HEMA-Desmodur N coatings show that they are equal and in some cases slightly superior to the corresponding DTDL catalyzed coatings. The same is true for the Model II controls. The gloss retention of a DTDL catalyzed 70 MMA/30 HEMA coating having a P/B ratio of 45/100 was similar to a coating having a P/B ratio of 64/100 (W-185 pigment).

The gloss retention of an 80 MMA/20 HEMA-Desmodur N coating catalyzed with DTDL was inferior to the corresponding 70 MMA/30 HEMA coating.

A DTDL catalyzed 70 EA/30 HEA-Desmodur N coating showed good gloss retention after 900 hours AWC-II exposure, but a fair degree of yellow/brownish spots were observed on the panel.

Overall, the appearance and adhesion of the exposed coatings were superior on Alodine Al 1200S substrate compared to the coatings on the primed substrates. This suggests that an effort to develop an improved primer (faster cure, better solvent resistance and adhesion) would be a worthwhile objective.

Florida exposed (6 months) Hylene® W and Desmodur N modified acrylic coatings (Exposure Series 21554 and 21608) are superior in gloss retention to the controls including 868-93774 and 926-9377 Lucite®, 93-21667 New Dulux®, 962-21667 acrylic enamel and 939-8539 modified acrylic lacquer, but equal to Desmodur N/Desmophen 650 coatings (Model I). The polyurethane modified acrylic coatings show stronger mildew formation than the Desmodur N/Desmophen 650 coatings (Model I). The use of several fungicides to eliminate this problem is being investigated.

VII. Evaluation of Desmodur N/Acrylic Clears

Various Desmodur N modified acrylic clears were formulated and evaluated as finishes for aluminum trailers and trucks. The 70 MMA/30 HEA-Desmodur N combination offers an attractive balance of properties including flexibility, impact resistance, hardness, rate of drying, and gel time of the solution. The results of the preliminary evaluation and the comparison with commercial controls are summarized in Table VII. None of the coatings show any water whitening after two-day immersion in tap water. The spotting of some of the experimental coatings is not considered a major problem because some of the commercial control coatings show the same phenomenon.

AWC-II and Florida exposure is in progress.

VIII. MEKO-Blocked Hylene® W

The preparation and evaluation of MEKO-blocked Hylene® W/ hydroxy acrylic prepolymer baking finishes was discussed in an earlier report.

The production of MEKO-blocked "Hylene" W (75% in Cellosolve acetate) was scaled-up to a 73 lbs. batch without difficulty and samples for evaluation are available.

The MEKO-Hylene® W adduct is a solid which occasionally crystallizes from the solution in the form of white crystals which melt at 120-135°C. The wide melting range is apparently due to the presence of several isomers.

IX. Scale-Up of Acrylic Prepolymers

Several acrylic prepolymerizations were scaled-up in a 20-gallon kettle at the Marshall Laboratory. The polymers scaled-up include 70 EA/30 HEMA, 70 MMA/30 HEMA, 70 MMA/30 HEA and 70 EA/30 HEA. No unusual problems were encountered and the batches were made available to interested parties for evaluation in polyurethane modified finishes and paints.

X. Field Testing

The following field tests were conducted with Desmodur N modified acrylics:

1) 70 EA/30 HEMA-Desmodur N (Ref. 12)

passenger car, off-white over sanded Dulux® (2 yrs. old), control Desmodur N/Desmophen 650 (Model II), conducted by G. C. Sun.

Observations: Satisfactory flow and sag resistance, no overspray melt-in problems, no solvent popping, some film distortion, tack-free in 15 min., tape-free in ~ 2 hrs. Model II control showed some solvent popping.

2) 70 MMA/30 HEMA-Desmodur N (Ref. 14)

A) passenger car, off-white over white "Corlar" primer, control Desmodur N/Desmophen 650 (Model II), conducted by G. C. Sun.

Observations: Application properties were good, no overspray melt-in problems, initial gloss somewhat lower than Model II control.

B) Diesel switcher, off-white over 825-006 zinc chromate epoxy primer, control Desmodur N/Desmophen 650 (Model II), conducted by E. R. Harkins (Ref. 15).

Observations: Good gloss but somewhat lower than Model II. Some sagging because of low viscosity, tendency to dry spray. The Model II control showed some surface bubbling and longer tack-free time.

Field tests planned for the near future:

1) 70 MMA/30 HEA

passenger car, off-white, control Dulux®
passenger car, metallic, control Desmodur N/Desmophen 650 (Model II), to be conducted by G. C. Sun.

2) 70 EA/30 HEA

topcoat for white shining Corfam®, will be conducted by G. C. Johnson, Old Hickory.

XI. Toxicity of Desmodur N Modified Acrylics

Marshall Laboratory (J. A. Antonelli) has taken responsibility in cooperation with Haskell Laboratory for testing of the urethane enamels to determine their toxicity relative to other well established products.

German toxicity reports indicate that Desmodur N has a low level of toxicity. The author of the German toxicity study (Ref. 12) is known to Haskell Lab and is considered a reliable source of information.

EXPERIMENTAL DETAILS

Scale-up of 70 MMA/30 HEA copolymerization (~ 18 gallons) (see Notebook 399E-125 and Marshall Lab Notebook 9335-24).

Equipment: 20-gallon stainless steel kettle

		Lbs.	
Charge:	MMA (Du Pont HA-9345)	46.00	
	HEA (Dow Chem. Co., 97%)	24.29	(adjust. for 100%)
	t-butyl peroctoate	2.46	(3.5% of monomer)
	n-butyl acetate	47.44	urethane grade
	Cellosolve acetate	15.67	
	ethyl acetate	7.19	
	t-butyl peroctoate-booster	0.144	(65.4 g.)

In order to remove a slight haze in the monomer mixture, 0.1% of "Celite Filter-Aid" is added with stirring and then the mixture is filtered through a cartridge filter.

The solvent is charged to the reaction vessel and heated to reflux (~ 118°C) with stirring under a blanket of nitrogen. To the refluxing solvent is added the monomer/catalyst mixture over a period of 4 hours. The reaction mixture is maintained at reflux for 1 hour and then the temperature is lowered to 100°C. Then half of the booster catalyst is added and the mixture is held at 100°C for an additional 30 minutes. Then the second half of the booster catalyst is added and the mixture is heated at 100°C for another 30 minutes. The polymer solution is then heated to reflux and maintained at reflux for 45 minutes. The polymer solution is cooled to ~ 50°C and let-down through six layers of cheesecloth.

We obtained 140.86 lbs. (98.4% of theor.) of a clear colorless polymer solution of Gardner-Holdt viscosity U/V at 49.6% solids.

Analytical Results:

% Polymer Solids - 49.7/49.5
% OH (solution) - 2.49/2.50 (corresponds to a 68.9 MMA/31.1 HEA copolymer molar ratio)
Acid No. (solution) - 2.33/2.37
% Vinyl (solution) - 0.215/0.211

MEKO-Blocked Hylene® W (Code No. 399E-68)
(see also Marshall Lab Notebook 9109-140)

Equipment: 20 gallon stainless steel kettle

		Lbs.	
Charge:	Hylene® W	33.00	
	MEKO (H-584)	22.05	(0.47% excess)
	Cellosolve acetate (ureth. grade)	18.33	
		73.38	

The MEKO-Cellosolve acetate solution is charged to the reaction vessel fitted with reflux condenser, water cooling, and nitrogen inlet. To this mixture the "Hylene" W is added with stirring under a blanket of nitrogen over a period of ~ 3.5 hours. The temperature is held below 50°C (reaction is exothermic) by intermittant water cooling. The reaction product is stirred for an additional hour after the "Hylene" W addition is complete and then letdown.

The reaction product is clear and nearly colorless and has a Gardner-Holdt viscosity of U (6.27 Poise). The solution contains 44.97% "Hylene" W or 14.39% NCO (if regenerated).

Scale-Up of 70 MMA/30 HEMA Polymerization

(Code No. 399E-89, see also Marshall Lab Notebook 9159-81)

Equipment: 20 gallon stainless steel kettle

		Lbs.
Charge:	MMA (Du Pont HA-9345)	32.41
	HEMA (Rohm & Haas, 96%)	18.79
	t-butyl peroctoate (4% of monomer)	.02
	n-butyl acetate	39.80
	Cellosolve acetate	11.40
	t-butyl peroctoate (0.2% of monomer)	0.10

The monomer/catalyst mixture was added to the refluxing solvent (128°C) with stirring under a slow stream of nitrogen over a period of 5 hours. Reflux was continued for 30 minutes after the addition was complete and then the booster catalyst dissolved in some distillate was added. The mixture was held at reflux for an additional 1.5 hours. The polymer solution was allowed to cool overnight and then let-down through felt filter.

We obtained a clear colorless polymer solution of Gardner-Holdt viscosity Z4/Z5 at 52.3% solids. At 40% solids, the Gardner-Holdt viscosity was K.

Analysis: % solids: 52.3; % OH (solution): 2.25
% vinyl: 0.75/0.80; M.W. (weight average): 33,000

Scale-up of 70 EA/30 HEA polymerization
(Code No. 399E-116, see also Marshall Lab Notebook

Equipment: 20 gallon stainless steel kettle

		Lbs.
Charge:	EA (H-72)	28.0
	HEA (Dow Chemical, 97%)	13.9
	Vazo® polymer catalyst (4% of monomer)	0.168
	Ethyl acetate (urethane grade)	21.0
	Xylene (H-583)	20.9
	Vazo® polymer catalyst-booster	0.084

The monomer/catalyst mixture was added to the refluxing solvent (89°C) with stirring under a slow stream of nitrogen over a period of 4 hours. Reflux was maintained for 45 minutes of the addition was completed and then the booster catalyst dissolved in some distillate was added. The mixture was held at reflux for an additional 1.5 hours, cooled to room temperature and let-down through cheesecloth.

The clear and nearly colorless polymer solution was characterized as follows:

% Polymer Solids - 49.4/49.4
Gardner-Holdt Viscosity - H (at 49.4% solids)
A1/A (at 40% solids)
% OH (polymer)- 4.89/4.90; Acid No. (polymer) 3.52/3.52
% Vinyl (solution) - 0.57/0.57

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TABLE I

Coating Solution:

10.0 g	polymer solids 70 MMA/30 HEMA (50% n-butyl acetate/propyl acetate 2/1)
0.009 g	50% silicone SF-1023 (0.05% act. ingr. of binder)
4.13 g	Desmodur N-75 (1.05 NCO/1 OH)
0.0043 g	DTDL (0.05% of binder)
8.0 g	solvent

(glass substrate, film thickness - 2 mil, room temperature cure)

Solvent	Gel Time (hrs)	Tack-Free (hrs)	Tape-Free (hrs)
Cellosolve Acetate	1	1/2	2
Propyl Acetate	1	1/2	2
Methyl Isobutyl Ketone	1 1/4	1/2	2
Diglyme	>7	3	>7
Anisole	1	3/4	2
Acetyl Acetone	36	1/2	4
Glyme	1	1/2	2
Dibutyl Ether	incompatible		
Dioxane	1	not determined	
2-Ethoxy Dihydropyrane	incompatible		

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TABLE II-A

EVALUATION OF KOJIC ACID POT-LIFE EXTENDER

(70 MMA/30 HEA-DESMODUR N)

Kojic Acid/ DTDL Mol. ratio	Gel Time (hrs)	Tack-Free (hrs)	Tape-Free (hrs)	KHN_{25} (1 day)
0.5/1	3	1	6	0.6
1/1	13	1	> 8 < 24	0.5
2/1	26	1	> 8 < 22	soft
4/1	36	1	> 22	soft
8/1	44	1 1/4	> 22	soft
DTDL only	1 1/4	3/4	3 1/2	0.7
DTDL AcAc	36	3/4	4	0.7

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TABLE II-B

EVALUATION OF POT-LIFE EXTENDERS

Coating Solution:
- 10.00 g pol. sol. 399E-89 (70 MMA/30 HEMA)
- 3.56 g Desmodur N (1.05 NCO/1 OH)
- 2.00 g n-butyl acet./Cellos. acet. - 50/50
- 2.50 g additive (13.8% of total)
- 0.00395 g DTDL (0.05% of binder)

(glass substrate, coating thickness ~ 2 mil)

Additive	Gel Time (hrs)	Tack-Free (hrs)	Tape-Free (hrs)	KHN_{25} 1 day	KHN_{25} 30' at 130°C	Cellosolve Acet. Res.
Acetyl Acetone	12	3/4	3	6.5	17.2	Excellent
Kojic Acid**	35	1/2	>4 <19	3.0	17.6	Excellent
Citric Acid	cloudy, gas evaoluation - discarded					
2-Butanol	1	discarded				
t-Butyl Alcohol	1	discarded				
Diacetone Alcohol	1	discarded				
Control (n-butyl ac./ Cellos. acet.- 50/50)	1	discarded				
*Control (n-butyl ac./ Cellos. acet.-50/50)	>31	3/4	>7 <23	Soft	16.9	Excellent

* no DTDL added
** 5% solution in MEK

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TABLE III

AMINE CURE OF DESMODUR N/DESMOPHEN 650

A = Alodine Al 1200S
B = Alclad Al primed with 818-012 Pretreatment Wash Primer and 825-8140 Corlar® Intermediate Coat White

Topcoat thickness ~ 1.5-2 mil

Catalyst	Substrate	Tack-Free (hrs)	Tape-Free (hrs)	KHN25 1 day	KHN25 4 days	P.H. 1 day	P.H. 4 days	Bump Test Conc.	Bump Test Conv.	Gloss 20°	Gloss 60°	Gel Time (hrs)
0.5 DABCO	A	3/4	2	12.6	15.8	F	F	60	10	88	94	< 4
	B	3/4	2	8.0	11.6	3B	2B	40	20	83	94	
0.35% DABCO	A	1 1/2	3	9.9	17.2	F	F	< 10	40	90	95	5
	B	1 1/2	3	5.4	15.4	3B	2B	40	40	88	95	
0.2% DABCO	A	2 1/4	6 1/2	5.8	18.7	HB	H	< 10	10	91	95	> 8
	B	2 1/4	6	2.2	15.5	< 6B	F	20	20	90	95	
0.1% NIAX AI	A	4	> 8									24
	B	4	> 8									
0.3% NIAX AI	A	3	~ 9									> 8
	B	3	~ 9									< 24
0.04% DTDL	A	1 1/4	3	2.3	15.0	3B	F	20	< 10	90	97	> 12
Control	B	1 1/4	3 1/2	1.3	11.8	< 6B	3B	20	10	90	97	< 22

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TABLE IV

VARIED HUMIDITY CURING OF 70 EA/30 HEMA-DESMODUR N COATINGS

Coating Compos: 70 EA/30 HEMA prepolymer
Desmodur N-75 (1.05 NCO/1 OH)
W-185 (P/B - 64)
DTDL (0.05% of binder)
Silicone (0.05% of binder)
Acetyl Acetone (18.5% of total)

Substrate: Alodine Al 1200S
Coating thickness ~ 2 mil

C. No.	Cure Temp. (°C)	Rel. Humid. (%)	Tack-Free (hrs)	Tape-Free (hrs)	KHN_{25}		Bump		Gloss	
					1 day	11 days	Conc.	Conv.	20°	60°
399E-81-I	23	23	1	2½	1.7	10	5	5	80	88
399E-81-II	23	50	1	2	1.7	4	7	5	80	87
399E-81-III	24.4	90	1	3	0.5	5	9	6	80	89

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TABLE V

EVALUATION OF 70 MMA/30 HEA CURED WITH EXCESS AND DEFICIENCY DESMODUR N-75

(Substrate: Alodine Al 1200 primed with white Corlar® 825-8136/V6-8392)
Topcoat film thickness ~ 2 mil

C. No. 399E-	Desmodur N-75 (% by Weight)*	Cure Temp. (°C)	Tack-Free (hrs)	Tape-Free (hrs)	KHN_{25} 1 day	KHN_{25} 12 days	Bump Conc.	Bump Conv.	Gloss 20°	Gloss 60°
81-IV	+ 1.5	24.4	1 1/2	3	2.0	14.0	9	6	76	88
81-V	+ 5.0	24.4	1 1/2	3	2.5	14.6	10	9	80	91
81-VI	+ 10.0	24.4	1 1/2	3	2.4	14.0	9	9	75	90
81-VII	- 10.0	24.4	1 1/4	2 1/2	3.4	13.0	8	6	78	90
81-VIII	+ 1.5	30 min. 130	after bake	after bake	18.4 after bake		7	5	62	84

* excess or deficiency over 1 NCO/1 OH ratio

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TABLE VI

EVALUATION OF WHITE (P/B-64) DESMODUR N MODIFIED ACRYLIC SYSTEMS

(Topcoat film thickness ~ 2 mil)

C. No.	Prepolymer Composition	Catalyst	Substrate	Tack-Free (hrs)	Tape-Free (hrs)	KHN25 1 day	KHN25 4 days	300 Hrs AWC-II	P.H. 1 day	P.H. 4 days	Bump Test Convex	Bump Test Concave	Gloss 20°	Gloss 60°	Gel Time (hrs)
399E-110A	70 MMA/30 HEMA	0.05% DTDL	Alod. Al. 1200S	3/4	3	5.6	11.9	21.1	H	H	<10	10	78	90	>8
			Primed Alclad	3/4	3	3.4	12.0	20.7	HB	F	<10	10	76	89	
399E-110B	70 MMA/30 HEMA	0.5% DABCO	Alod. Al. 1200S	1 1/2	3 1/2	14.4	—	22.8	H	-	<10	<10	78	89	>9
			Primed Alclad	1 1/2	4	9.3	—	20.4	F	-	10	40	66	86	
399E-111E	70 MMA/30 HEMA 1,4-butane diol	0.05% DTDL	Alod. Al. 1200S	3/4	3	3.3	13.4	22.8	B	F	<10	20	76	89	>8
			Primed Alclad	3/4	3	2.0	11.5	21.7	6B	B	<10	10	75	89	
399E-111F	70 MMA/30 HEMA 1,4-butane diol	0.5% DABCO	Alod. Al. 1200S	3/4	3 1/2	11.2	16.7	21.1	F	F	10	<10	82	91	>8
			Primed Alclad	1	3 1/2	5.3	14.3	21.1	5B	2B	<10	20	80	91	
399E-110D	70 MMA/30 HEMA - P/B - 45	0.05% DTDL	Alod. Al. 1200S	3/4	3 1/2	5.6	—	19.5	H	-	<10	<10	79	89	>8
399E-110C	80 MMA/20 HEMA	0.05% DTDL	Alod. Al. 1200S	3/4	4	4.0	—	21.1	B	-	<10	<10	81	90	>8
			Primed Alclad		4	3.2	—	20.4	B	-	<10	20	77	89	
399E-111G	70 EA/30 HEA	0.05% DTDL	Alod. Al. 1200S	1 1/4	<2	soft	1.8	8.2	6B	4B	>60	>60	81	90	>8
			Primed Alclad	1 1/4	<2	soft	1.7	7.0	soft	6B	>60	>60	81	90	
9226-90	Desmodur N/ Desmophen 650	0.04% DTDL	Alod. Al. 1200S	1 1/2	4	2.3	15.0	22.1	F	F	10	60	93	96	>8
			Primed Alclad	1 1/2	4	1.3	11.8	20.7	2B	HB	10	10	90	94	
399E-117II	Desmodur N/ Desmophen 650	0.35% DABCO	Alod. Al. 1200S	1 1/2	3	9.9	17.2	21.1	F	F	<10	40	90	95	5
			Primed Alclad	1 1/2	3	5.4	15.4	20.1	3B	2B	40	40	88	95	
399E-117III	Desmodur N/ Desmophen 650	0.2% DABCO	Alod. Al. 1200S	2 1/4	6 1/2	5.8	18.7	—	HB	H	<10	10	91	95	>8
			Primed Alclad	2 1/4	6	2.2	15.5	—	<6B	F	20	20	90	95	

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TABLE VII

EVALUATION OF DESMODUR N MODIFIED ACRYLIC CLEARS

(Substrate H-5052/H-32 Al Alloy; Film Thickness ~ 1 mil)

Lacquer/Enamel	Tack-Free (hrs)	Tape-Free (hrs)	KHN_{25} 1 day	KHN_{25} 4 days	Bump Conc.	Bump Conv.	Water Soak	Gasol. Resist.	Gel Time (hrs)	Comments
100D Clear (Du Pont)	< 1	5-6	1.2	6.2	20	20	strong spotting	good	—	—
Duracryl DCA-400 Clear[1] LSR-9044 (Ditzler)	1/2	1	5.5	5.5	10	20	strong spotting	poor (tacky)	—	—
Nextel 107-M10 Clear[2] LSR-9045 (3M)	1	> 17	soft	0.7	20	< 10	O.K.	fair (tacky)	—	too soft, long drying time
1234 Clear (Du Pont)	1/2	1/2	5.9	6.7	20	20	strong spotting	poor (swelling)	—	—
Desmodur N/Desmophen 650-DABCO (Du Pont)	1	4-5	13.4	19.8	60	60	O.K.	excell.	24	Coating solution turns cloudy after 3 hrs. Some adhes. failure
Desmodur N/Desmophen 650-DTDL (Du Pont)	1	3	2.7	19.2	60	60	O.K.	excell.	30	Coating solution turns cloudy after 8 hrs.
70 MMA/30 HEA-DTDL 399E-125	1/2	3	—	8.3[3]	60	60	medium spotting	excell.	> 14 < 22	—
70 MMA/30 HEA-DABCO 399E-125	1/2	3	—	16.9[3]	20	60	strong spotting	excell.	7	Some adhesion failure on edges after water soak
70 MMA/30 HEMA-DTDL 399E-89	< 1	1 1/2	11.5	16.7	10	10	medium spotting	excell.	6	Coatings show slight orange peel. Adhesion failure after water soak
70 EA/30 HEA-DTDL 399E-116	3/4	1	elast.	elast.	60	60	slight spotting	excell.	6 1/2	—
70 EA/30 HEMA-DTDL 399E-64	3/4	1	elast.	6.0	60	60	O.K.	excell.	5 1/2	—

1) Reduced 1:1 with methyl isoamyl ketone
2) Reduced 1:1 with T-3864
3) Measured after 3 days

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ABSTRACT

The development and evaluation of two-package white and clear Desmodur N modified acrylic coatings are discussed.

The laboratory and scale-up production of hydroxy bearing acrylic prepolymers, including catalyst and solvent studies, are described. The acrylic prepolymers were formulated into white paints and clear coating compositions and their properties were investigated. Weather-Ometer and Florida exposure results of these coatings are reported.

The amine catalysis of Desmodur N modified acrylics and Desmophen 650 is described.

GLOSSARY

Desmodur N-75 - hexamethylene diisocyanate biuret (75%) (Bayer, A. G.)

Desmophen 650 - hydroxy polyester (Bayer, A. G.)

MMA - methyl methacrylate

HEA - hydroxyethyl acrylate

HEMA - hydroxyethyl methacrylate

EA - ethyl acrylate

DABCO - triethylenediamine

DTDL - dibutyltin dilaurate

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