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Report No. IITRI-C6180-6
(Final Report)

STUDIES OF PARAMETERS AFFECTING THE INTERFACIAL BOND STRENGTH OF DIFFICULT TO REMOVE LINEAR POLYURETHANE AIRCRAFT PAINT SYSTEMS

Naval Air Systems Command

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STUDIES OF PARAMETERS AFFECTING THE INTERFACIAL BOND STRENGTH OF DIFFICULT TO REMOVE LINEAR POLYURETHANE AIRCRAFT PAINT SYSTEMS

April 22, 1969 to April 21, 1970

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FOREWORD

This is Report No. IITRI-C6180-6 (Final Report) on IITRI Project C6180, Contract No. N00019-69-C-0410 entitled "Studies of Parameters Affecting the Interfacial Bond Strength of Difficult to Remove Linear Polyurethane Aircraft Paint Systems" covering the period from April 22, 1969 to April 21, 1970.

Personnel who contributed to this project include Mrs. M. Gould, Mr. T. Yamauchi and Dr. K. Baburao.

Data are recorded in IITRI logbooks No. C19020, C19585 and C19705.

Respectfully submitted,

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STUDIES OF PARAMETERS
AFFECTING THE INTERFACIAL BOND STRENGTH OF DIFFICULT
TO REMOVE LINEAR POLYURETHANE AIRCRAFT PAINT SYSTEMS

ABSTRACT

The present study led to the conclusion that the effectiveness of a paint stripper did not depend primarily on the paint polymer swelling abilities of the component organic solvents. It appears that some other parameters, for example, evolution of hydrogen in the case of Turco-5469, have to come into play before the solvents in the paint remover can effectively swell the paint polymer thereby causing the stripping of linear polyurethane paint systems. Furthermore, from the scanning electron micrographs it is surmised that there are enough pinholes and voids on the paint surface to enable the penetration and permeation of the common organic solvents.

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STUDIES OF PARAMETERS
AFFECTING THE INTERFACIAL BOND STRENGTH OF DIFFICULT
TO REMOVE LINEAR POLYURETHANE AIRCRAFT PAINT SYSTEMS

I. INTRODUCTION

Navy aircraft require a periodic removal of old protective organic coatings to assess the damage, if any, done by marine environment to the substrate metal. It is important that this routine maintenance and overhaul of naval equipment be carried out as efficiently and economically as possible with a minimum of difficulty due to the chemicals in the paint removers. The advent of new and more effective adhesive paint systems resulted in the use of organic solvents and chemicals which often affect the substrate metal and, additionally, pollute the environment. The purpose of research work performed during the contract period was to gain better understanding of the parameters affecting the interfacial bond strength of difficult to remove linear polyurethane aircraft paint systems. The knowledge acquired from these studies would be useful in formulating better and more efficient paint strippers comprising organic solvents and chemicals which do not harm the aircraft substrate metal and which pose fewer environmental problems.

In the present investigations, we studied the following parameters which are likely to influence the removal of linear polyurethane aircraft finish by organic solvent based paint strippers:

A. Swelling of paint polymer systems

B. Physical nature of linear polyurethane finished paint surface

C. Evolution of hydrogen gas during paint stripping

D. Chemical nature of linear polyurethane finished paint surfaces.

The study of dimensional changes in the paint polymer systems, when in contact with organic solvents, enabled us to select nearly fifteen solvents for inclusion into the paint stripper formulation within the period covered by this report. During the present study we did not make serious efforts to formulate new experimental paint strippers. In this final report are summarized our findings and the results obtained in the course of the research program.

II. RESULTS AND DISCUSSION

A. Swelling of Paint Polymer Systems

The aircraft paint system consists of two organic coatings: primer of epoxy resin (e.g., Mil-P-23377) and a top coat of polyurethane (e.g., 910-177, Super Desothane Enamel, activator and 821-010, Super Desothane Enamel, white). In order to study the swelling behavior of individual as well as binary paint polymers with and without aircraft metal as substrate, we prepared the following test materials with the polymer paints mentioned earlier:

1. Test panel with epoxy primer on the surface activated aircraft metal substrate
2. Test panel with polyurethane finish on the surface activated aircraft metal substrate
3. Test panel with polyurethane over epoxy primer on the surface activated aircraft metal substrate
4. Paint film of epoxy undercoating
5. Polyurethane paint film
6. Paint film of polyurethane on epoxy primer.

All the above paint systems were subjected to a baking cycle of 90 hr at 150°F, 10 hr at 300°F, 2 hr at 350°F and half an hour at 400°F. This baking cycle is supposed to simulate the aging of the paint surface on the aircraft when ready for a paint stripping job. The paint polymer films are generally obtained by spraying the paint onto a glass plate and lifting the paint layer with a razor blade. Alternately, the paint

polymer was sprayed onto a sheet of tin foil and the tin foil substrate was afterwards amalgamated with mercury to leave behind a thin film of the paint system.

The use of laboratory-made paint polymer films instead of the test paint panels as experimental materials offered certain advantages. In our earlier work on biocompatible paint strippers,[1] we found that there were two disadvantages in employing the test paint panels for experimentation. First, the cause for the ineffectiveness of a candidate solvent was not always clear; it could be due to either poor penetration and permeation of the solvent into the paint layer or lack of intrinsic capacity of the solvent to swell the paint polymer. Secondly, even if swelling did take place, there was no method available to measure the swelling and quantify the results. In the present work, the use of paint polymer films, instead of the test paint panels, overcame these difficulties.

Then, we turned our attention to the selection of solvents for use as swelling agents in the present study. It is neither necessary nor practical to measure the swelling ability of each one of these organic compounds. For the preliminary screening purposes, we resorted to the concept of solubility parameters.[2] In 1916, Hildebrand[3] advanced the idea, in the course of developing his theories on the solubility of non-electrolytes, that a molecule will be attracted most effectively by other molecules that have the same internal pressure. This concept suggests that if a solute molecule is surrounded by solvent

molecules that have the same internal pressure it will be an ideal solution. On the other hand, if the internal pressures are sufficiently different, then the molecules with the greater internal pressure will cling to themselves and exclude from among themselves the molecules with the lesser internal pressure and immiscibility will result. In between these extremes, a mixture of two components with differing internal pressures will result in a lessening of the attractive forces in the molecules and this will cause partial pressures greater than predicted by Raolut's law,* thus a volume increase on mixing and an endothermic heat of mixing. Satchard[4] introduced the concept of cohesive energy density into Hildebrand's theories, identifying this quantity with the energy of vaporization per ml. Hildebrand and his coworkers[5] gave the term

$$\left[\frac{\Delta E}{V}\right]^{1/2}$$

the square root of the internal pressure of each component, the name "solubility parameter" and the symbol, δ. A similarity of solubility parameters is, therefore, an indication that the compounds will form a solution. In the course of this development, however, it has also become apparent that the attraction forces between organic molecules are of four distinguishable types, namely, (a) London (dispersion) forces, (b) Keesom forces (dipole-dipole), (c) Debye forces (dipole-

*Raoult's Law: The vapor pressure of a substance is proportional to its molecular fraction.

induced dipole), and (d) Lewis forces (acid-base forces of which, by far, the most important is hydrogen bonding). Because the solubility parameter is a gross measure of all these forces and because these different types of forces do not interact effectively, a similarity of solubility parameters do not always assure miscibility. For the same reasons, a range of values instead of a particular value is quoted for the solubility parameter.

The development of the solubility parameter concept proved to be a great step forward in the selection of solvents for polymers. Some of the applications of this concept in the polymer chemistry cover paint formulations, economic choice of solvent, plasticizer selection, inventory control and compatibility studies. However, many cases have been found in which a polymer will not dissolve in a solvent in spite of the fact that they have similar solubility parameters. This is, as has been mentioned earlier, due to the lack of an equal balance of London, Keesom and hydrogen bonding forces in spite of the similarity of solubility parameters. This led Burrell[6] to classify solvents into three categories, viz. weakly hydrogen bonded, moderately hydrogen bonded and strongly hydrogen bonded whereas later workers[7,8] developed a three dimensional approach to solubility. A recent book on solubility and compatibility includes a list of solvents classified on the basis of solubility parameters as well as the effective solubility parameters of a number of resins and polymers.[9]

The relevance of the solubility parameters to the problem on hand stems from the anticipation that these concepts will provide a rationale for the selection of solvents for incorporation into the paint strippers. The grounds for such expectations come from the work in the polymer field on solubility parameters. To illustrate the point, Burrell and coworkers,[2] during their studies on the effect of coatings and inks on the swelling of application rolls, have shown that the maximum swelling of polymers like polyurethane and Thiokol occurred when the solubility parameters of solvents were similar to those of the polymers. It is well known that the purpose of either the solvent or cosolvent in a paint stripper is not to effect a complete solution of the paint system but to swell the macromolecular paint layer. In line with this reasoning a large number of solvents were used in preliminary screening for their effects on baked polyurethane, epoxy and polyurethane on epoxy paint systems. In these screening experiments, we followed visually the changes occurring in the paint films and the results are given in Tables 1 to 4 along with pertinent observations. The solvents listed in Table 1 belong to the weakly hydrogen bonded class whereas those in Tables 2 and 3 represent the moderately hydrogen bonded and strongly hydrogen bonded categories, respectively. Furthermore, these candidate solvents in Tables 1 to 3 are listed in the increasing order of their solubility parameters. The solvents, which were chosen on a chemical intuitive basis, were screened for their

Table 1

PRELIMINARY SCREENING OF THE SOLVENTS
FOR THE EFFECTIVE SOLUBILITY PARAMETERS OF BAKED
POLYURETHANE, EPOXY AND POLYURETHANE ON EPOXY PAINT SYSTEMS
(Class I: Weakly Hydrogen Bonded Solvents)

No.	Solvent	Solubility* Parameter, δ	Hydrogen* Bonding, γ	Dipole* Moment, μ	Observations
		Hydrocarbon Solvents			
1.	n-Decane	6.6	0	0	No effect
2.	n-Pentane	7.0	0	0	No effect
3.	Isoprene	7.4	-	-	No effect
4.	n-Heptane	7.4	0	0	No effect
5.	n-Octane	7.6	0	0	No effect
6.	Methylcyclohexane	7.8	0	0.3	No effect
7.	Turpentine	8.1	-	-	Some softening of the epoxy coating
8.	Cyclohexane	8.2	0	0	No effect
9.	Dipentene	8.5	1.5	0	No effect
10.	Ethylbenzene	8.8	1.5	0.6	Good softening of the epoxy primer; slight swelling of the polyurethane and the polyurethane on epoxy films
11.	Xylene (commercial)	8.8	4.5	0.4	Slight swelling of epoxy primer
12.	Toluene	8.9	4.5	0.4	Slight swelling of epoxy primer
13.	Benzene	9.2	0	0	No effect
14.	Tetralin	9.5	-	-	No effect
		Halogenated Solvents			
15.	iso-Butyl chloride	8.1	1.5	2.1	Slight softening of the epoxy primer
16.	n-Amyl chloride	8.3	1.5	2.2	No effect
17.	n-Propyl chloride	8.5	-	-	No effect
18.	Carbon tetrachloride	8.6	0	0	No effect
19.	n-Butyl bromide	8.7	1.5	2.0	Slight softening of the epoxy primer
20.	1,2-Dichloropropane	9.0	1.5	1.6	No effect

Table 1 (cont.)

No.	Solvent	Solubility* Parameter, δ	Hydrogen* Bonding, γ	Dipole* Moment, μ	Observations
21.	Chloroform	9.3	1.5	1.2	Slight softening of the epoxy primer
22.	Trichloroethylene	9.3	-	-	No effect
23.	Pentachloroethane	9.4	-	-	Slight softening of the polyurethane film
24.	Tetrachloroethylene	9.4	-	-	No effect
25.	Chlorobenzene	9.5	1.5	1.6	No effect
26.	Methylene chloride	9.7	1.5	1.5	Slight softening of the epoxy primer
27.	1,1,2,2-Tetrachloroethane	9.7	-	-	Very good swelling of the three polymer coatings
28.	Dichloroethyl ether	9.8	-	-	Good softening of the epoxy primer; slight softening of the polyurethane and the polyurethane on epoxy paint systems
29.	Ethylene dichloride	9.8	1.5	1.1	Slight softening of the polyurethane film
30.	o-Dichlorobenzene	10.0	-	-	No effect
31.	Dibromoethylene	10.1	-	-	Slight softening of all the three paint systems
32.	1,2-Dibromoethane	10.4	-	-	No effect
33.	α-Bromonaphthalene	10.6	-	-	No effect
		Nitrogen Solvents			
34.	Nitrobenzene	10.0	2.8	4.3	Slight softening of the epoxy primer
35.	Butyronitrile	10.5	7.7	4.0	No effect
36.	Nitropropane	10.7	2.5	3.7	No effect
37.	Propionitrile	10.8	7.7	4.0	No effect
38.	Nitroethane	11.1	2.5	3.6	No effect
39.	Nitromethane	12.7	2.5	3.4	No effect
		Sulfur Solvents			
40.	Carbon disulfide	10.0	0	0	No effect

*Taken from reference 9.

Table 2

PRELIMINARY SCREENING OF THE SOLVENTS
FOR THE EFFECTIVE SOLUBILITY PARAMETERS OF BAKED
POLYURETHANE, EPOXY AND POLYURETHANE ON EPOXY PAINT SYSTEMS
(Class II: Moderately Hydrogen Bonded Solvents)

No.	Solvent	Solubility* Parameter, δ	Hydrogen* Bonding, γ	Dipole* Moment, μ	Observations
			Ethers		
1.	Dibutyl ether	7.1	11.0	1.2	No effect
2.	Ethylbutyl ether	7.2	11.7	1.2	No effect
3.	Diethyl ether	7.4	13.0	1.2	No effect
4.	Anisole	9.9	7.0	1.4	No effect
5.	1,4-Dioxane	9.9	9.7	0	No effect
			Esters		
6.	Ethyl benzoate	8.2	6.3	2.0	Slight softening of the epoxy primer
7.	sec-Butyl acetate	8.2	-	-	No effect
8.	iso-Propyl acetate	8.4	8.6	1.9	No effect
9.	n-Propyl butyrate	8.4	-	-	Slight softening of the epoxy primer
10.	n-Amyl acetate	8.4	9.0	1.8	Slight softening of the epoxy primer
11.	Ethyl n-butyrate	8.5	-	-	Slight softening of the epoxy primer
12.	Propyl propionate	8.5	7.0	1.9	No effect
13.	n-Butyl propionate	8.6	8.4	1.9	Slight softening of the epoxy primer
14.	n-Butyl formate	8.7	7.5	1.9	Slight softening of the epoxy primer
15.	Cellosolve Acetate (Diethylene glycol monomethyl ether acetate)	8.7	9.4	1.8	No effect
16.	n-Propyl acetate	8.8	8.6	1.9	Slight softening of the epoxy primer
17.	Methyl n-butyrate	8.9	-	-	No effect
18.	Ethyl acetate	9.1	8.4	1.8	No effect
19.	Methyl propionate	9.3	8.4	1.9	No effect
20.	Methyl acetate	9.6	8.4	1.7	No effect

Table 2 (cont.)

No.	Solvent	Solubility* Parameter, δ	Hydrogen* Bonding, γ	Dipole* Moment, μ	Observations
21.	Methyl formate	10.2	8.4	1.9	No effect
22.	Methyl benzoate	10.4	6.3	1.9	No effect
23.	Phenyl acetate	10.4	7.7	1.9	No effect
24.	Dimethyl phthalate	10.7	-	-	No effect
	Ketones				
25.	Diisobutyl ketone	7.8	8.4	2.7	No effect
26.	Methyl nonyl ketone	7.8	7.7	2.7	No effect
27.	Diisopropyl ketone	8.0	8.4	2.7	No effect
28.	Methylisoamyl ketone	8.3	7.4	2.7	Slight softening of the epoxy primer
29.	Methyl n-hexyl ketone (2-octanone)	8.4	-	-	No effect
30.	Diethyl ketone	8.8	7.7	2.7	No effect
31.	Methylpropyl ketone	8.9	8.0	2.7	No effect
32.	Isophorone	9.1	-	-	Slight softening of the epoxy primer
33.	Methylcyclohexanone	9.3	-	-	Very good softening of the epoxy primer
34.	Methylethyl ketone	9.3	7.7	2.7	No effect
35.	Cyclohexanone	9.9	11.7	2.7	Good softening of the epoxy primer; slight softening of the polyurethane on epoxy paint system
36.	Acetone	10.0	9.7	2.9	Not effective
	Ether and Mixed Alcohols				
37.	Butyl cellosolve	8.9	13.0	1.6	Slight softening of the epoxy primer
38.	Diacetone alcohol	9.2	13.0	2.5	Good softening of all the three polymer systems
39.	n-Butyl lactate	9.4	7.0	1.9	Good softening of the epoxy primer; slight softening of the polyurethane on epoxy
40.	Ethyl lactate	10.0	8.4	1.8	No effect

Table 2 (cont.)

No.	Solvent	Solubility* Parameter, δ	Hydrogen* Bonding, γ	Dipole* Moment, μ	Observations
		Nitrogen Solvents			
41.	Benzonitrile	8.4	7.7	4.4	Slight softening of the epoxy primer
42.	N,N-Diethylacetamide	9.9	12.3	2.0	Very good softening of all the three paint systems
43.	Acrylonitrile	10.5	5.7	3.8	No effect
44.	N,N-Dimethylacetamide	10.8	12.3	2.0	Good softening of the epoxy primer; slight softening of the polyurethane and the polyurethane on epoxy paint systems
45.	Aniline	11.8	18.1	1.5	No effect
46.	Acetonitrile	11.9	6.3	3.9	No effect
47.	Dimethylaniline	12.0	14.3	1.5	No effect
		Sulfur Solvents			
48.	Dimethylsulfoxide	12.9	7.7	4.0	Slight softening of all the three paint systems
49.	Dipropylsulfone in methylene chloride	11.3	7.7	4.5	Slight softening of all the three paint systems
		Halogenated Solvents			
50.	sec-Butyl bromide	8.1	-	-	No effect
51.	n-Butyl bromide	8.7	1.5	2.0	No effect
		Miscellaneous			
52.	Mesitylene	8.8	-	-	No effect
53.	Diethylcarbonate	8.8	5.0	1.2	No effect
54.	Mesityl oxide	9.0	9.7	2.7	Good softening of the epoxy primer; slight softening of the polyurethane on epoxy paint system
55.	Propylene oxide	9.2	10.0	1.8	Good softening of all the three paint systems
56.	Dimethylcarbonate	9.9	4.9	1.0	No effect
57.	1,2-Propylene carbonate	13.3	4.9	1.0	No effect
58.	Ethylene carbonate	14.7	4.9	1.0	No effect
59.	γ-Butyrolactone	15.5	9.7	2.7	Slight softening of the epoxy primer

*Taken from reference 9.

Table 3

PRELIMINARY SCREENING OF THE SOLVENTS
FOR THE EFFECTIVE SOLUBILITY PARAMETERS OF BAKED
POLYURETHANE, EPOXY AND POLYURETHANE ON EPOXY PAINT SYSTEMS
(Class III: Strongly Hydrogen Bonded Solvents)

No.	Solvent	Solubility* Parameter, δ	Hydrogen* Bonding, γ	Dipole* Moment, μ	Observations
			Alcohols		
1.	Diethylene glycol	9.1	-	-	No effect
2.	2-Ethyl hexanol	9.5	18.7	1.7	No effect
3.	Isoamyl alcohol	10.0	-	-	No effect
4.	Methylisobutyl carbinol	10.0	18.7	1.7	No effect
5.	n-Octyl alcohol	10.3	18.7	1.7	No effect
6.	2-Ethylbutanol	10.5	-	-	No effect
7.	t-Butyl alcohol	10.6	-	-	No effect
8.	n-Heptyl alcohol	10.6	-	-	Slight softening of the epoxy and polyurethane on epoxy paint systems
9.	n-Hexyl alcohol	10.7	18.7	1.7	No effect
10.	n-Amyl alcohol	10.9	-	-	No effect
11.	n-Butyl alcohol	11.4	18.7	1.7	No effect
12.	Cyclohexanol	11.4	18.7	1.7	No effect
13.	Isopropyl alcohol	11.5	-	-	No effect
14.	n-Propyl alcohol	11.9	18.7	1.7	No effect
15.	Benzyl alcohol	12.1	18.7	1.7	Slight softening of all the three paint systems
16.	Furfuryl alcohol	12.5	-	-	No effect
17.	Ethyl alcohol	12.7	18.7	1.7	No effect
18.	Ethylene glycol	14.2	20.6	2.3	No effect
19.	Methyl alcohol	14.5	18.7	1.7	No effect
20.	Glycerol	16.5	-	-	No effect
21.	Water	23.4	39.0	1.8	No effect
			Nitrogen Solvents		
22.	N,N-Diethylformamide	10.6	11.7	2.0	Good softening of all the three paint systems
23.	Pyridine	10.7	18.1	2.2	Slight softening of all the three paint systems
24.	N,N-Dimethylformamide	12.1	11.7	2.0	Good softening of all the three polymer paint systems
25.	N-Ethylformamide	13.9	12.0	2.0	Very good softening of the epoxy primer; good softening of the polyurethane and the polyurethane on epoxy paint systems
26.	N-Methylformamide	16.1	12.0	2.0	Slight softening of all the three polymer paint systems

*Taken from reference 9.

Table 4

PRELIMINARY SCREENING OF THE SOLVENTS CHOSEN ON CHEMICAL INTUITIVE BASIS FOR THE EFFECTIVE SOLUBILITY PARAMETERS OF BAKED POLYURETHANE, EPOXY AND POLYURETHANE ON EPOXY PAINT SYSTEMS

No.	Solvent	Observations
	Nitrogen Compounds	
1.	4-Chlorobutyronitrile	Slight softening of the epoxy primer
2.	Dibenzylamine	No effect
3.	Diethylene triamine	Slight softening of the epoxy and the polyurethane coatings
4.	N,N-Dimethylaniline	No effect
5.	Di-n-propylamine	No effect
6.	N-Ethyl-N-β-hydroxyl ethylaniline	Slight softening of all the three polymer paint systems
7.	N-Ethylmorpholine	Good softening of the epoxy primer; slight softening of the polyurethane on epoxy
8.	Ethyl nitrate	No effect
9.	1-Fluoro-2,4-dinitro-benzene	No effect
10.	2,6-Lutidine	Slight softening of all the three polymer paint systems
11.	1-Methyl-2-piperidone	Very good softening of the epoxy primer; slight softening of the polyurethane and the polyurethane on epoxy paint systems
12.	N-Methylpyrrole	Very good softening of the epoxy and polyurethane polymer paint systems; good softening of the polyurethane on epoxy
13.	2,2',2"-Nitriloethanol	No effect
14.	β-Isopropoxypropionitrile	No effect
15.	Pyrrole	Very good softening of the epoxy and polyurethane polymer paint systems; good softening of the polyurethane on epoxy

Table 4 (cont.)

No.	Solvent	Observations
16.	2-Pyrrolidone	No effect
17.	1,1,3,3-Tetramethylurea	Good softening of all the three polymer paint systems
18	N-Vinyl pyrrolidone	Slight softening of all the three polymer paint systems
	Halogenated Compounds	
19.	1-Bromopropane	No effect
20.	4-Chloro-1-butanol	Good softening of the epoxy and polyurethane paint system; slight softening of the polyurethane on epoxy primer
21.	1,4-Dibromobutane	No effect
22.	1,2-Dibromopropane	No effect
23.	Dichloroisopropyl ether	Good softening of the epoxy; good softening of the polyurethane on epoxy primer
24.	2,3-Dichlorooctafluorobutane	No effect
25.	Hexachloroacetone	No effect
	Phosphorus Compounds	
26	Hexamethylphosphoramide	Good softening of the epoxy polymer
27.	Triethyl phosphate	Slight softening of the epoxy polymer
28.	Trimethylallylphosphate	No effect
29.	Trimethylphosphate	No effect; slight swelling of polyurethane film
	Hydroxy Compounds	
30.	1,4-Butane diol	No effect
31.	Isobutanol	No effect
32.	2-Ethyl-1,3-hexanediol	Slight softening of the epoxy primer

Table 4 (cont.)

No	Solvent	Observations
33.	4-Ethylphenol	Good softening of the polyurethane film; slight softening of the epoxy and polyurethane on epoxy paint systems
	Esters	
34.	Ethyl acrylate	No effect
35.	Ethyl citrate	No effect
36.	Ethylethoxypropionate	No effect
37.	Ethylorthoformate	No effect
38.	2-Methoxy-1-methyl ethylacetate	No effect
	Ethers	
39.	iso-Butyl vinyl ether	No effect
40.	Methylol	No effect
41.	Vinyl-n-butyl ether	Good softening of the epoxy and polyurethane paint systems; slight softening of the polyurethane on epoxy primer
	Carbonyl Compounds	
42.	iso-Butylaldehyde	No effect
43.	Diacetone	Good softening of the epoxy and polyurethane on epoxy paint systems; slight softening of the polyurethane
44.	Propiophenone	No effect
	Hydrocarbons	
45.	2,2-Dimethylbutane	No effect
46.	Indene	No effect

Table 4 (cont.)

No.	Solvent	Observations
47.	Triethylbenzene	No effect
		Miscellaneous
48.	N,N-Diethylphenyl-carbonate	No effect
49.	Hexamethyldisiloxane	No effect
50.	Trimethoxy boroxime	No Effect

effective solubility parameters and are listed in alphabetical order in Table 4. Even though this preliminary screening of solvents by visual means is somewhat arbitrary and subjective, it has enabled us to narrow down the number of solvents for further detailed studies on swelling measurements. After a careful consideration of available methods, we adopted the Rapid Swelling Test[10] developed in the past in our laboratories for this purpose. This method consists of measuring the changes in length, width and thickness of a polymer specimen before and after contact with a solvent under a microscope. The increases in percentage areas (ΔA) and volumes (ΔV) represent the magnitude of polymer swelling. Instead of measuring the dimensional changes of the polymer at its equilibrium swelling point (which might require many hours), we determined the changes in length, width and thickness of the polymer after 30 minutes. The data on the thickness of the polymer (after contact with the solvent) are somewhat unsatisfactory because of the presence of adhering solvent to the polymer film. The results of swelling measurements with the baked polyurethane, epoxy and polyurethane on epoxy paint polymer films in terms of ΔA, ΔV and rate of swelling are given in Table 5.

The lack of knowledge about many of the physicochemical properties of paint polymers such as chemical composition, degree of polymerization, extent of crosslinking, molecular weights and others precludes any serious discussion on the

Table 5

DIMENSIONAL CHANGES IN THE BAKED POLYURETHANE (A), EPOXY (B) AND POLYURETHANE ON EPOXY (C) PAINT FILMS WHEN IN CONTACT WITH SELECTED SOLVENTS

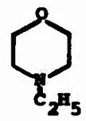
No.	Solvent with Chemical Structure	Solubility* Parameter, δ	Hydrogen* Bonding, γ	Dipole* Moment, μ	Paint Film	Swelling Characteristics: % Increase in Area, ΔA	Swelling Characteristics: % Increase in Volume, ΔV	Observations
	I. Nitrogen Solvents							
1.	N,N-Diethylacetamide	9.9	12.3	2.0	A	37.9	32.6	Minor change after 25 min
	$CH_3C(=O)N(C_2H_5)_2$				B	58.7	25.0	Slow swelling in 5 min
					C	-	-	
2.	N,N-Diethylformamide	10.6	11.7	2.0	A	52.2	59.4	Within 6 min polymer folds; after 8 min polymer flattens
	$HC(=O)N(C_2H_5)_2$				B	59.2	90.2	Slow swelling
					C	46.4	65.2	Slow swelling
3.	Diethylenetriamine				A	37.9	54.5	Polymer folds within 5 min; after 10 min polymer flattens
	$H_2NCH_2CH_2NHCH_2CH_2NH_2$				B	42.7	65.9	
					C	-	-	No action
4.	N,N-Dimethylacetamide	10.8	12.3	2.0	A	50.1	75.6	Folding begins within 2 min and buckles in center within 4 min
	$CH_3C(=O)N(CH_3)_2$				B	51.2	16.7	Slow expansion in 2 min
					C	48.7 46.4	63.7 67.5	Slow expansion in 4 min
5.	N,N-Dimethylformamide	12.1	11.7	2.0	A	47.3	62.3	Swelling begins within 2 min; no folding occurs
	$HC(=O)N(CH_3)_2$				B	39.2	60.0	Rapid swelling in 2 min
					C	36.0 41.0	58.3 65.9	Slow expansion in 5 min
6.	N-Ethylmorpholine				A	-	4.9	No change in 10 min
					B	36.5	32.0	Rapid folding
					C	-	-	No action

Table 5 (cont.)

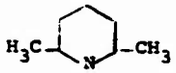
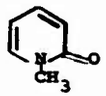
No.	Solvent with Chemical Structure	Solubility* Parameter, δ	Hydrogen* Bonding,	Dipole* Moment, μ	Paint Film	Swelling Characteristics % Increase in Area, ΔA	% Increase in Volume, ΔV	Observations
7.	2,6-Lutidine				A	45.3	55.6	Slow swelling; polymer folds within 8 min; no change after 25 min
					B	53.8	81.1	Rapid swelling
					C	36.8	71.0	Very slow expansion
8.	N-Methylformamide	16.1	12.0	2.0	A	44.0	81.6	Begins to fold within 25 min; polymer flattens after 4 min
	$H_3CHNCNH_2$ (O)				B	20.8	22.8	Very slow swelling
					C	16.3	14.0	Negligible swelling
9.	N-Methyl-2-piperidone				A	56.7	90.2	Folds within 5 min; flattens after 8 min
					B	55.8	91.6	Slow expansion
					C	54.0	85.9	Swelling began after 5 min
10.	N-Methylpyrrole				A	34.6	38.6	Within 30 sec folds appear; flattens after 2 min
					B	36.5	49.5	Very slow swelling
					C	45.8	69.0	Very slow swelling
11.	Morpholine				A	40.0	83.3	Folds within 3 min
					B	67.5	156.7	Slow expansion in 6 min
					C	-	-	Negligible swelling
12.	Pyridine	10.7	18.1	2.2	A	51.6	54.8	Folds and buckles within 2 min; flattens after 3 min
					B	60.8	112.0	Immediate and rapid expansion
					C	44.0 44.0	72.8 76.6	Rapid expansion

Table 5 (cont.)

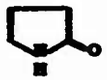
No.	Solvent with Chemical Structure	Solubility* Parameter, δ	Hydrogen* Bonding, γ	Dipole* Moment, μ	Paint Film	Swelling Characteristics: % Increase in Area, ΔA	Swelling Characteristics: % Increase in Volume, ΔV	Observations
13.	Pyrrole				A	63.8	76.0	Folds and buckles within 30 sec; flattens after 2 min
					B	47.8	79.8	Rapid expansion
					C	46.1 44.0	69.3 71.7	Folds within 1 min
14.	Pyrrolidine				A	54.7	89.0	Folds and buckles within 1.5 min; flattens after 3 min
					B	51.2	78.7	Rapid expansion
					C	48.8 46.8	87.9 82.5	Folds and swells after 20 min
15.	2-Pyrrolidone 				A	-	6.5	No change within 15 min
					B	-	27.0	Negligible swelling
					C	-	-	No action
16.	1,1,3,3-Tetramethylurea $(CH_3)_2N\overset{O}{C}N(CH_3)_2$				A	63.8	83.8	Folds within 5 min; flattens after 8 min
					B	62.2	106.4	Rapid swelling
					C	-	-	No action
17.	N-Vinylpyrrolidone (containing 0.1% NaOH as inhibitor)				A	57.8	88.5	Folds within 3 min; buckles within 9 min
					B	48.8	76.2	The paint film folds; slow swelling
					C	-	-	Negligible swelling
	II. Halogenated Solvents							
18.	4-Chloro-1-butanol $ClCH_2CH_2CH_2CH_2OH$				A	65.8	98.3	Gradual swelling; no folding or buckling
					B	27.6	48.4	Very slow expansion
					C	-	-	No action

Table 5 (cont.)

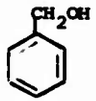
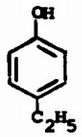
No.	Solvent with Chemical Structure	Solubility* Parameter, -	Hydrogen* Bonding, γ	Dipole* Moment, μ	Paint Film	Swelling Characteristics % Increase in Area, ΔA	% Increase in Volume, ΔV	Observations
19.	Dichloroethylether				A	28.9	35.6	Folds within 6 min; flattens after 10 min
	$CH_2ClCHClOCH_2CH_3$				B	-	-	No action
					C	15.5	17.0	Very slow swelling
20.	Ethylenedichloride	9.8	1.5	1.1	A	37.9	45.7	Rapid swelling within 45 sec
	$ClCH_2CH_2Cl$				B	34.6	41.8	Very slow swelling
					C	35.8 32.0	56.6 45.5	Very slow swelling
21.	Methylene chloride	9.7	1.5	1.5	A	54.4	70.7	Folds and buckles within 10 sec
	CH_2Cl_2				B	44.0	77.4	Swelling starts immediately
					C	40.0 38.3	64.5 48.1	Rapid swelling; curls
22.	1,1,2,2-Tetrachloroethane	9.7			A	58.7	94.3	Folds within 5 min; flattens after 7 min
	$Cl_2CHCHCl_2$				B	87.6	168.5	Rapid and immediate expansion
					C	83.0 94.3	128.8 169.9	Rapid and immediate expansion
	III. Alcohols and Phenols							
23.	Benzyl alcohol	12.1	18.7	1.7	A	51.8	58.0	Folds and buckles within 5 min; flattens after 8 min
					B	56.2	81.1	Very slow swelling
					C	35.3	56.3	Very slow swelling
24.	4-Ethylphenol				A	108.9	265.6	Rapid and best swelling; folds within 3 min; flattens after 12 min
					B	96.0	187.5	Slow expansion after 4 min
					C	Shrinks 90.4	4.6 177.0	Slow expansion

Table 5 (cont.)

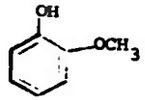
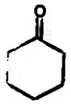
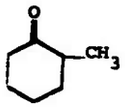
No.	Solvent with Chemical Structure	Solubility* Parameter, -	Hydrogen* Bonding, γ	Dipole* Moment, μ	Paint Film	Swelling Characteristics: % Increase in Area, ΔA	% Increase in Volume, ΔV	Observations
25.	Guaiacol 				A	79.6	132.7	Folds within 8 min; flattens after 20 min
					B	-	-	No effect
					C	-	-	
				IV. Ketones				
26.	Cyclohexanone 	9.9	11.7	2.7	A	-	-	No effect
					B	47.4	38.4	Very slow swelling
					C	-	-	No effect
27.	Diacetone $(CH_3)_2\overset{OH}{C}CH_2\overset{O}{C}CH_3$				A	30.4	30.6	Very slow swelling
					B	34.6	60.0	Very slow swelling
					C	-	-	No effect
28.	Mesityl oxide $(CH_3)_2C{=}CH\overset{O}{C}CH_3$	9.0	9.7	2.7	A	31.6	33.6	Slow swelling
					B	34.6	48.7	Slow swelling
					C	17.8 30.0	21.0 35.4	Slow swelling
29.	Methylcyclohexanone 				A	-	6.25	Negligible swelling
					B	44.0	51.3	Very slow swelling
					C	-	-	No effect
				V. Miscellaneous				
30.	n-Butylvinylether $CH_3CH_2CH_2CH_2OCH{=}CH_2$				A	39.2	61.2	Very slow swelling
					B	57.1	54.0	Slow expansion
					C	14.6	22.6	No effect

Table 5 (cont.)

No.	Solvent with Chemical Structure	Solubility* Parameter,	Hydrogen* Bonding,	Dipole* Moment, μ	Paint Film	Swelling Characteristics: % Increase in Area, ΔA	Swelling Characteristics: % Increase in Volume, ΔV	Observations
31.	Dimethylsulfoxide $(CH_3)SO$	12.9	7.7	4.0	A	46.5	68.7	Swells within 5 min; no folding or buckling
					B	20.8	26.6	Very slow swelling
					C	39.2 41.4	51.3 47.3	Very slow swelling
32.	Ethylbenzene	9.8	1.5	0.6	A	34.5	91.2	Folds within 9 min; flattens after 12 min
					B	22.0	40.1	No change in 3 min; slow swelling afterwards
					C	-	-	No effect
33.	Propylene oxide CH_3CHCH_2 (O)	9.2	10.0	1.8	A	36.9	46.2	Rapid swelling without folding in 15 sec
					B	36.5	49.1	Rapid swelling
					C	50.0 29.4	55.6 38.0	Rapid swelling
34.	Turco-5469				A	99.2	173.7	Folds and buckles immediately
					B	-	-	Immediate folding of the film
					C	-	-	Disintegrates the paint film

*Taken from Reference 9.

relationships between the swelling of macromolecular paint films and the physical and chemical properties of the solvents. Moreover, the missing data on solubility parameters, hydrogen bonding characteristics and dipole moments for some of the solvents in Table 5 render the task still more difficult. The data presented in Table 5, however, lend themselves to some broad practical conclusions. The effective solubility parameters for the baked polyurethane, epoxy and polyurethane on epoxy paint polymers are 9.7 to 9.8 as judged from the occurrence of maximum swelling (Figures 1, 2 and 3). This indicates that the future search for effective organic solvents for inclusion into paint strippers for linear polyurethane aircraft paint system could be confined to those solvents whose solubility parameters are around 9.7 to 9.8. Another salient feature of the solvents which are effective swelling agents is the presence of nitrogen atom in the molecule. It is quite possible that the lone pair of electrons on the nitrogen coordinates effectively either with the inorganic metal ion of the pigment or some other grouping in the paint molecular lattice and causes the easy swelling of the paint polymer. The attention was, therefore, focussed on nitrogen compounds, especially heterocyclic compounds, as candidate materials for inclusion into the paint strippers. Other information which could be gleaned from the swelling measurement data is about the presence and influence of "acidic hydrogen" or "active hydrogen" on the effectiveness of a solvent as a swelling agent. Thus, 4-ethylphenol, benzyl alcohol,

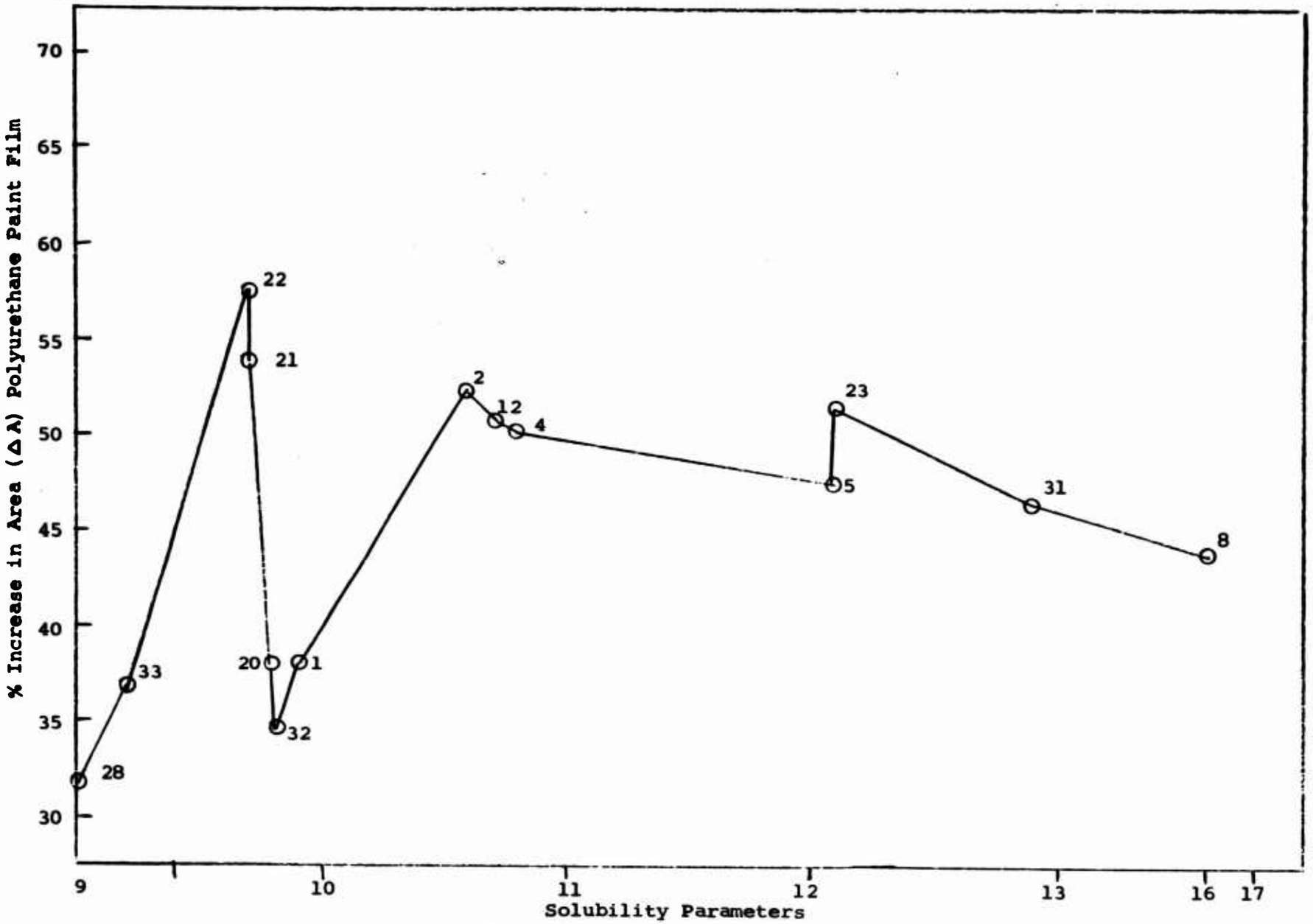


Figure 1

SWELLING BEHAVIOR OF POLYURETHANE PAINT SYSTEM
(The numbers refer to the solvents in Table 5)

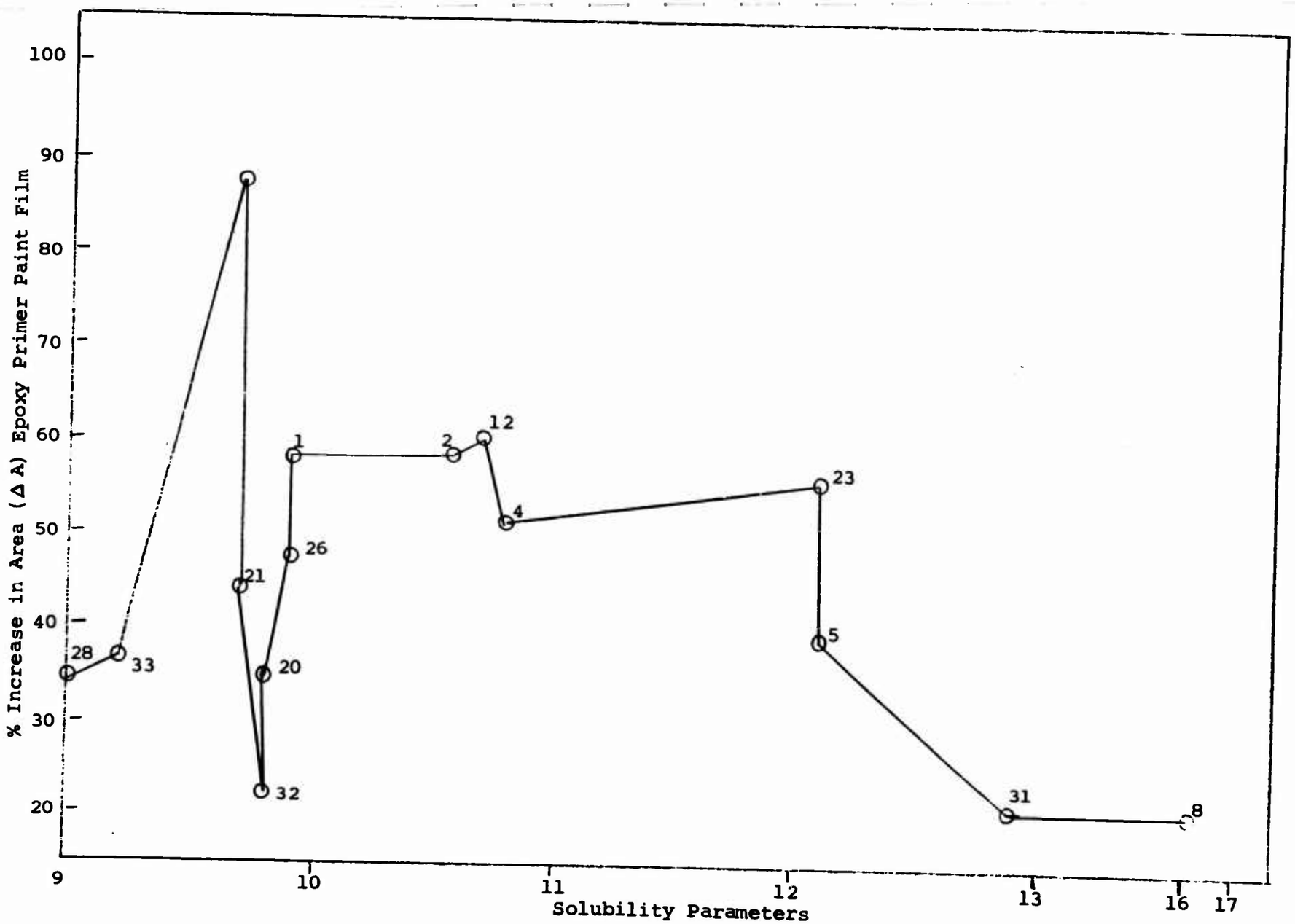


Figure 2

SWELLING BEHAVIOR OF EPOXY PRIMER PAINT SYSTEM
(The numbers refer to the solvents in Table 5)

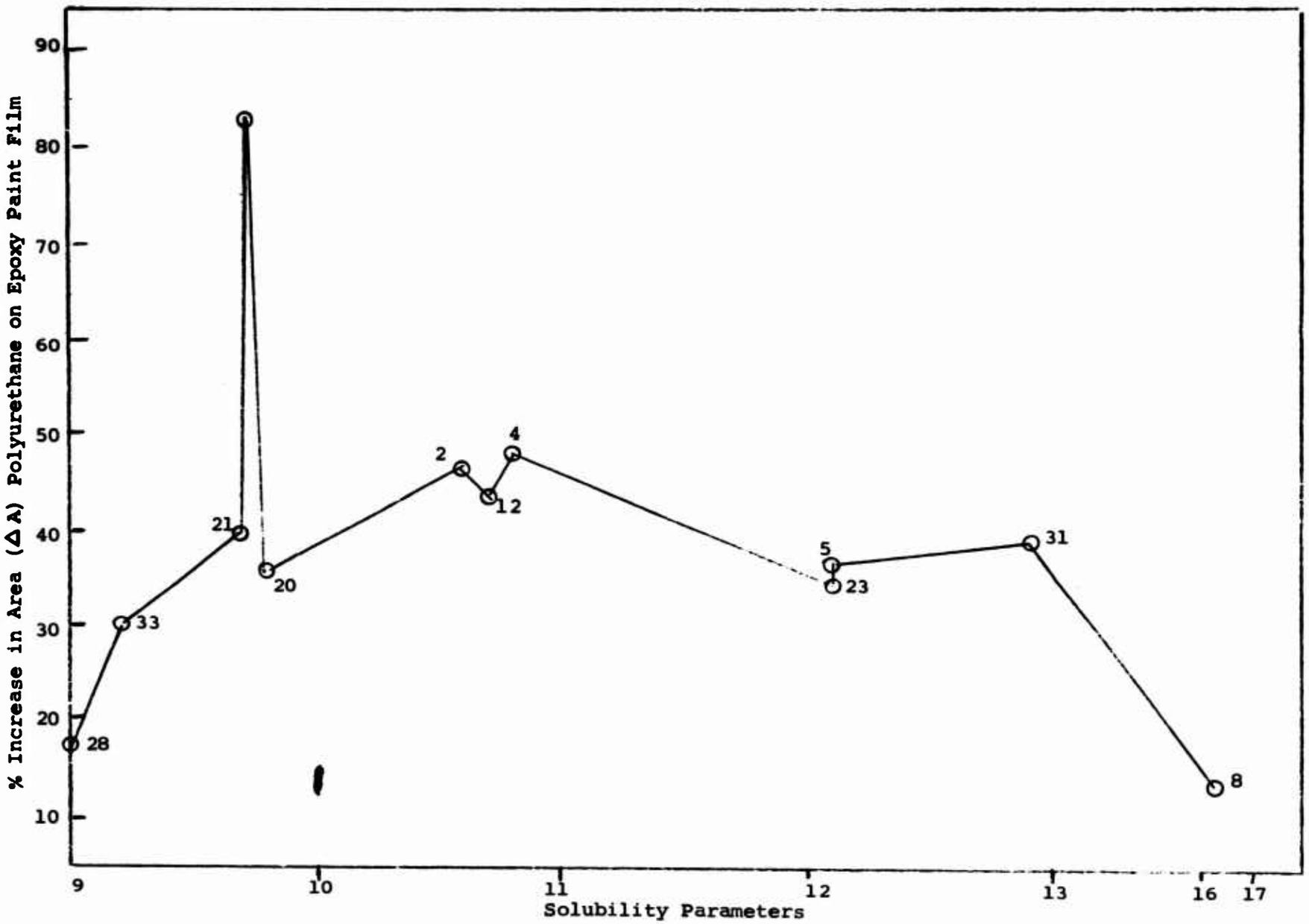
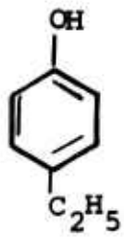


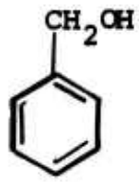
Figure 3

SWELLING BEHAVIOR OF POLYURETHANE OVER EPOXY PAINT SYSTEM
(The numbers refer to the solvents in Table 5)

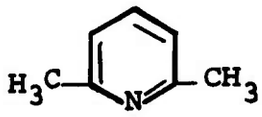
2,6-lutidine, pyrrolidine have this labile hydrogen in their molecules.



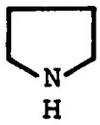
4-Ethylphenol



Benzyl alcohol



2,6-Lutidine



Pyrrolidine

The relationship between the labile hydrogen present in the molecule and the ability of solvent to swell the polymer is not clearly understood at this time.

Besides enabling us to draw the above conclusions, the swelling measurements (Table 5) resulted in a list of candidate solvents (Table 6) which are likely to be successful candidates for paint stripping action provided that swelling of the paint system is synonymous with the paint removal process. In ranking these solvents we not only considered the changes in polymer films in terms of $\triangle A$, but also the rate of change. In later experiments, we examined the swelling behavior of these promising solvents with baked epoxy, polyurethane and polyurethane on epoxy paint systems over the aircraft metal as substrate.

Table 6

LIST OF CANDIDATE SOLVENTS LIKELY TO BE EFFECTIVE IN THE PAINT STRIPPER FORMULATIONS*

Benzyl alcohol (23)
N,N-Diethylacetamide (1)
N,N-Diethylformamide (2)
Dimethylformamide (5)
Dimethylsulfoxide (31)
Ethylene chloride (20)
4-Ethylphenol (24)
2,6-Lutidine (7)
Mesityl oxide (28)
Methylene chloride (21)
N-Methyl-2-piperidone (9)
N-Methylpyrrole (10)
Propylene oxide (33)
Pyridine (12)
Pyrrole (13)
Pyrrolidine (14)
1,1,2,2-Tetrachloroethane (22)

*The numbers in parentheses refer to encircled solvents in Table 5.

The solvents had no visible effect on any of the three paint finishes. At this stage, we want to recall our past work wherein we established the importance of permeation and penetration of the solvents in the paint stripping action.[1] To rule out the possibility of the lack of permeation and penetration as one of the causes for the ineffectiveness of the solvents examined in the present work, we made pinholes on the paint surface and reinvestigated the swelling with the solvents. Even then, none of these solvents had any appreciable effect on any of the three paint finishes. These results indicate that swelling of the paint systems by solvents, in itself, is not strong enough to overcome the adhesive forces between the metal substrate and paint layers and initiate the crucial paint wrinkling process. This hypothesis derives further support from our experiments on the swelling of baked polyurethane on epoxy primer over a glass plate as substrate. None of the solvents had any visible effect on the paint coating in these experiments; however, when artificial pinholes were made on the paint surface and again tested with the solvents, most of the organic solvents wrinkled the organic coating. Another interesting aspect of these studies is that it required a long period (2 to 24 hr) for these solvents to wrinkle the paint layer.

B. Physical Nature of Linear Polyurethane Finished Paint Surface

In the course of our past work,[1] we recognized that the history and aging as well as surface topography (especially the presence or absence of pinholes) greatly influence the effectiveness of a paint stripper. To obtain a general understanding of the physical nature of the organic coating, we examined a polyurethane finished panel under a scanning electron microscope (SEM). The use of scanning electron microscope for this purpose has a number of advantages. Important among them are resolution (100-600A), enormous depth of focus and contrast. The contrast formation in the scanning electron microscopy is reflected in the micrographs. These surface photographs appear as contrasts between darkness and illumination, black and white. The illuminated or white segments in these micrographs indicate the presence on the surface of the specimen of protrusions or obstacles which scatter the electrons. On the other hand, black sections, dark spots or diffused illumination in these surface photographs denote the presence of deep crevices or voids on the surface under examination. The principle of contrast formation is illustrated in Figure 4.[11] The incident electron beam strikes the surface and the sphere resting on the surface which casts a shadow from Q to R. The collector on the right cannot receive any signal from the QR region since no primary electrons reach that area. Consequently, this region appears as a dark segment on the micrograph. The region PQ, however, will produce secondary electrons that are attracted

to the collector and follow indirect paths due to the electrostatic field in front of the collector. As a consequence, this region appears as diffusely illuminated parts in the surface photographs. The rest of the surface as well as the top of the sphere are seen directly by the collector. This is reflected in the surface photographs as follows: the sphere will appear as a white protrusion and the surface without imperfections will be seen as white background; the deep crevices and holes appear as dark portions.

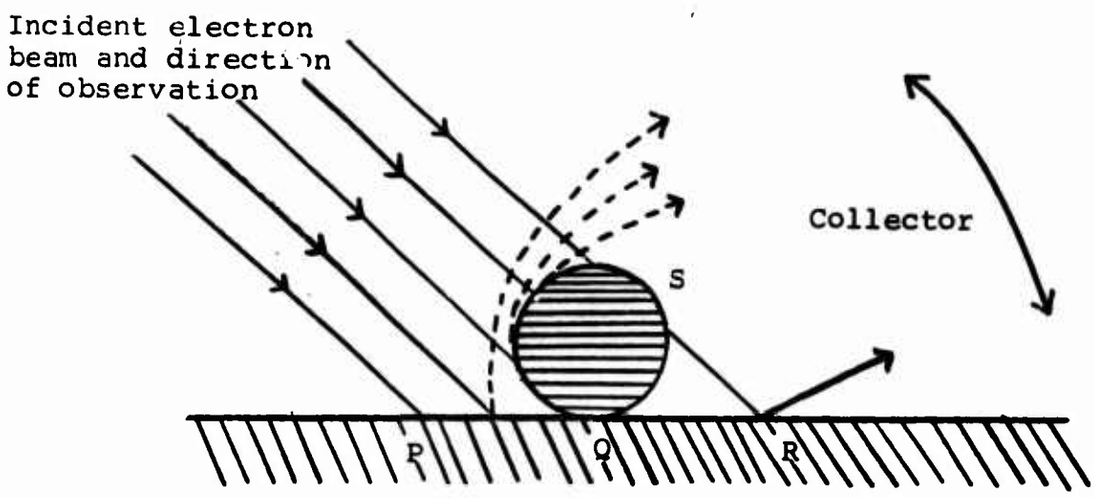


Figure 4

THE ORIGIN OF CONTRAST IN SCANNING ELECTRON MICROSCOPE
(Taken from Reference 11)

To prepare the specimens for study under SEM, the samples are first coated with gold. In the case of the polished metal surface, however, coating with gold was omitted (Figure 5; X1000). Due to the presence of oxides, the micrograph was poorly resolved and, therefore, shows nothing of importance, except the cracks and crevices on the metal surface.

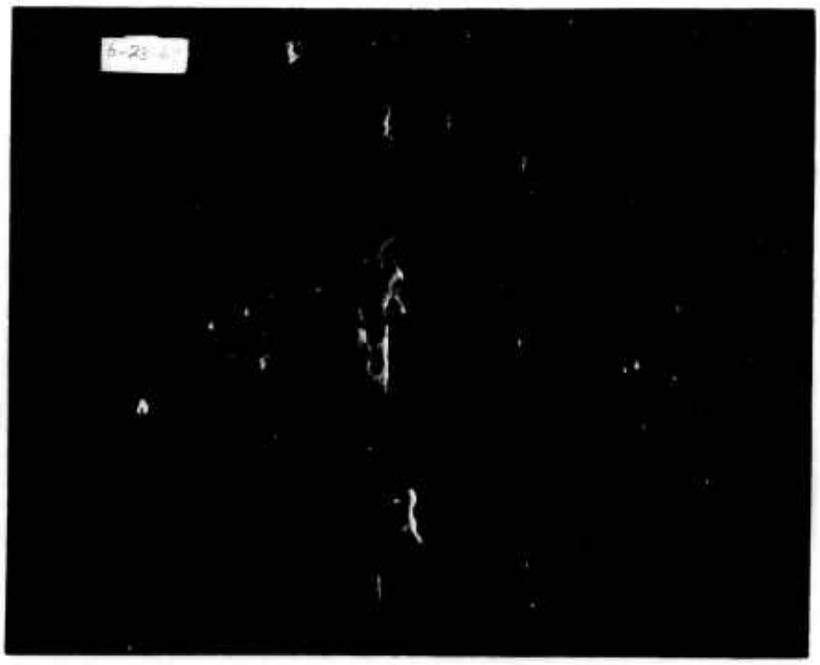


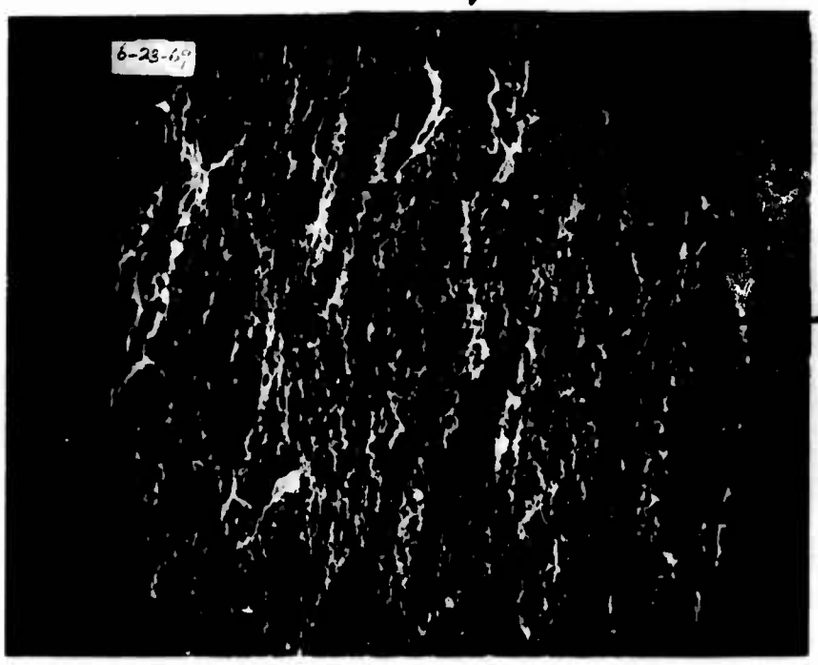
Figure 5

MICROSTRUCTURE OF POLISHED METAL SURFACE (X1000)

Surface photographs were obtained by cementing the specimen to a copper disc using a conductive paste, metalizing with gold by vacuum deposition.

Figure 6 (X1000) is the surface photograph of a specimen of a polyurethane coated panel.

See Figure 7



See Figure 8

Figure 6

DETAILS OF POLYURETHANE AIRCRAFT FINISH
OVER AN EPOXY PRIMER (X600)
(Paint Thickness 1.35 to 1.8 mil)

In this micrograph, the imperfections on the paint surface are manifested as hollows of a honeycomb structure. These hollows, due to pinholes and voids on the paint surface, are dramatically magnified in Figures 7 and 8 which are blown-up regions of Figure 6. It has to be pointed out that the incident electron beams in SEM have the energy to penetrate through a surface depth of 50-70A (5×10^{-7} cm) whereas the thickness of the paint system is in the order of 1.35 to 1.8 mil (3.43 to 4.57×10^{-3} cm). Consequently, in these surface photographs we are probably looking only at the top coating of polyurethane. The white protrusions in these micrographs could be due to either inorganic pigment in the polyurethane matrix or segments of polyurethane macromolecule.

Figure 7

DETAILS OF POLYURETHANE AIRCRAFT FINISH
OVER AN EPOXY PRIMER (X3000)
(Paint Thickness 1.35 to 1.8 mil)

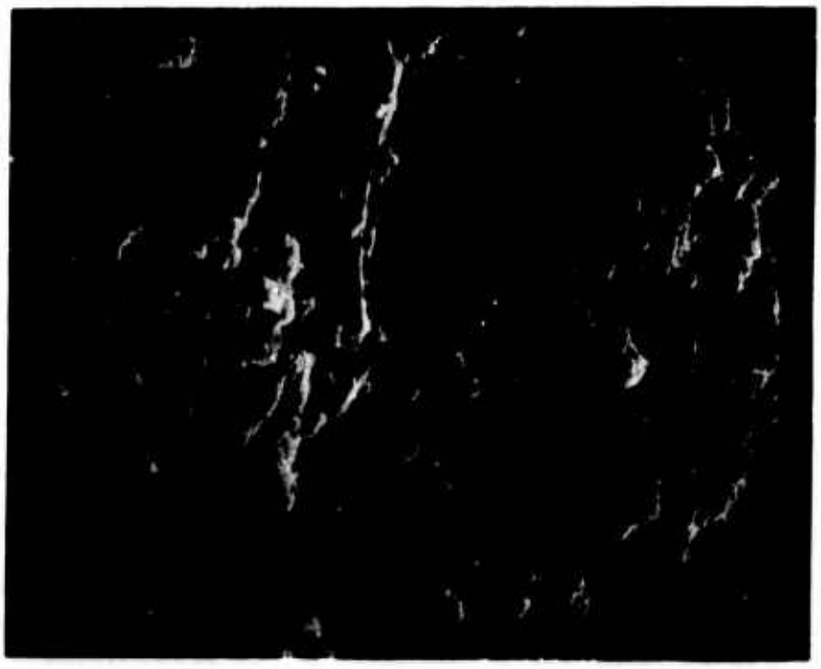
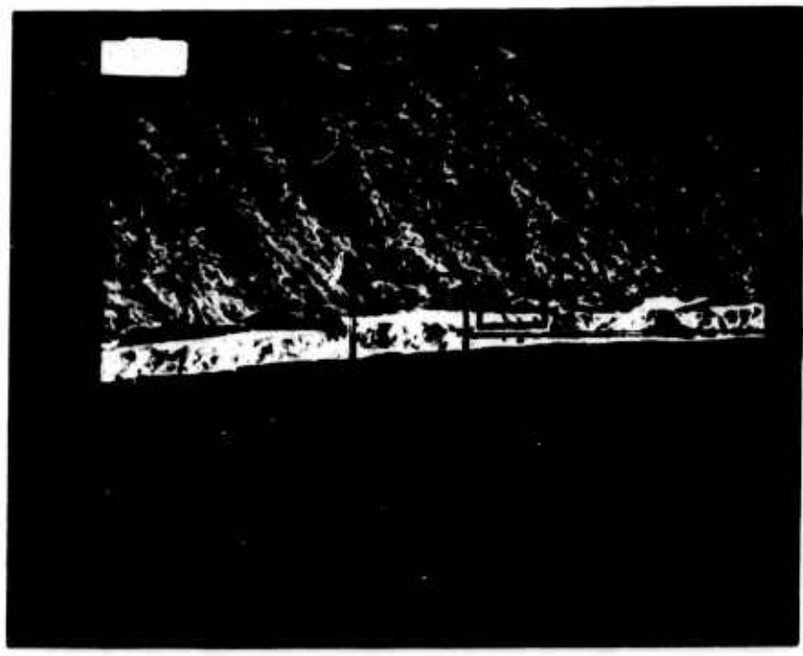


Figure 8

DETAILS OF POLYURETHANE AIRCRAFT FINISH
OVER AN EPOXY PRIMER (X6000)
(Paint Thickness 1.35 to 1.8 mil)

The photographs of the fractured polyurethane panels, on the other hand, show the interfaces of the metal and paint system. In Figure 9 (X100), the metal appears as a darker area and the paint system as the lighter section. The voids, appearing as black patches along the ragged edges, indicate the cohesive failure of the paint system, i.e., where the metal and paint system either were not bonded or were torn apart. In Figure 10 (X3000), an enlargement of one of these voids, the interfaces of the metal-paint system are more clearly delineated.



See Figure 10

See Figure 11

Figure 9

FRACTURED SURFACES OF POLYURETHANE FINISHED PANELS (X100)

Figure 10

FRACTURED SURFACES OF POLYURETHANE FINISHED PANELS
(X3000)

Another section of Figure 9 is enlarged (Figure 11; X600) to show the paint system in more detail.

See Figure 12

Figure 11

FRACTURED SURFACES OF POLYURETHANE FINISHED PANELS (X600)

A further enlargement of a section of Figure 11 shows the intimate details of the paint system (Figure 12, X3000).

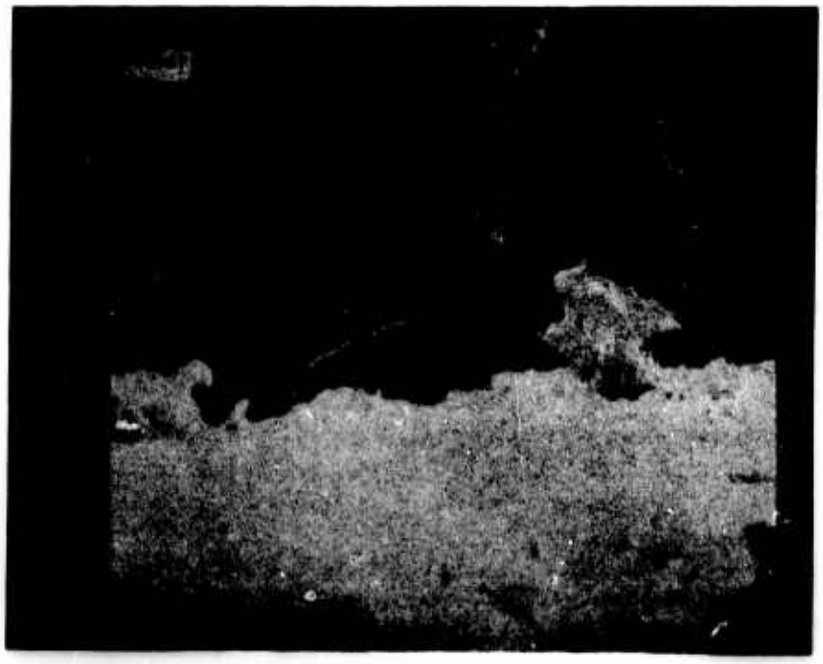


Figure 12

FRACTURED SURFACES OF POLYURETHANE FINISHED PANELS (X3000)

In summary, from the study of surface photographs, we find that a large number of pinholes and voids do exist on the surface of polyurethane top coating. A logical conclusion drawn from these findings is that penetration by organic solvents is not impeded by the polyurethane top coating, provided the size of the solvent molecules is small enough to pass through the holes on the surface coating. We have to stress here that these findings and conclusions pertain only to the polyurethane top coating and cannot be extrapolated either to the epoxy under coating or polyurethane-epoxy paint system.

Besides the foregoing work with the scanning electron microscope, we have also conducted some experiments to study the feasibility of using liquid crystals to determine the effectiveness of experimental paint stripper formulations on a routine basis. The preliminary results were so discouraging[12] that we did not pursue this line of research any further.

C. Evolution of Hydrogen Gas During Paint Stripping

One of the problems which plagues the removal of linear polyurethane aircraft paint systems using the paint strippers in current use (e.g., Turco-5469) is the incidence of hydrogen embittlement results in disastrous delayed failures in the metals unless its effects are remedied, a procedure which makes the paint removal jobs laborious and uneconomical. The embittlement is generally caused by hydrogen segregated in the microcracks of the stressed region of the metal.[13] It has

become important, therefore, to find out whether this occluded hydrogen could arise from the reactions of paint strippers either with the substrate metal or the paint polymers. For this purpose, we analyzed the effluent gases from the action of Turco-5469 with the paint test panels and other paint polymers for hydrogen by means of gas chromatography (Table 7). We found that hydrogen did, indeed, evolve by the action of Turco-5469 both on the test paint panels and the surface activated aircraft metal substrate. The prolonged contact of Turco-5469 with these panels seems to enhance the liberation of hydrogen over a period of time (see Figures 13 and 14). On the other hand, the action of Turco-5469 on the baked polyurethane film did not give rise to hydrogen. In contrast, the interaction of Turco-5469 with either polyurethane on the baked epoxy primer or epoxy primer coating seems to liberate minute quantities of hydrogen (Figure 15). The evidence obtained on this aspect is too scanty to arrive at any definite conclusions. We have also considered the possibility that the water used to flush off the stripped paint might catalyze the evolution of hydrogen. Our results indicate that the addition of water to the samples did in no way affect the liberation of hydrogen (see Table 6).

The foregoing demonstration of the evolution of hydrogen during the paint stripping action has an important bearing on the mechanism of paint removal. The process of paint removal by organic solvent paint strippers can be followed by the physical changes taking place on the surface of high polymer

Table 7

GAS CHROMATOGRAPHIC MONITORING OF HYDROGEN ON PORAPAK Q COLUMN IN THE EFFLUENT GASES FROM THE ACTION OF TURCO-5469 WITH POLYURETHANE PAINT SYSTEMS

Origin of Gas Samples	Retention Time (In Min)		
	Hydrogen	Nitrogen	Oxygen
1. Air	-	9.4	11.3
2. Purified hydrogen	4.1	-	-
3 3 g of Turco 5469	-	9.7	11.3
	-	9.7	11.3
4. 3 g of Turco 5469	-	9.6	11.2
and 1 ml of water	-	9.6	11.2
5. 3 g of Turco 5469	4.1	9.7	11.2
and 9.3 g of test	4.1	9.7	11.2
panel	4.1	9.7	11.2
	4.1	9.7	11.2
6. 3 g of Turco 5469,	4.1	9.7	11.2
9.4 g of test panel	4.1	9.7	11.2
and 1 ml of water	4.1	9.7	11.2
	4.1	9.7	11.2
7. 3 g of Turco 5469	4.1	9.7	11.2
and 7.6 g surface	4.1	9.7	11.2
activated aircraft	4.1	9.7	11.2
metal substrate	4.1	9.7	11.2
8. 3 g of Turco 5469,	4.1	9.7	11.2
7.6 g of surface	4.1	9.7	11.2
activated aircraft	4.1	9.7	11.2
metal substrate	4.1	9.7	11.2
and 1 ml of water			
9. 3 g of Turco 5469	-	9.9	11.4
and 0.2 g of baked	-	9.9	11.4
polyurethane paint	-	9.9	11.4
film	-	9.9	11.4

Table 7 (cont.)

Origin of Gas Samples	Retention Time (In Min) Hydrogen	Nitrogen	Oxygen
10. 3 g of Turco 5469 and 0.2 g of baked epoxy primer	-	9.9	11.4
	4.2	9.8	11.3
	4.3	9.8	11.3
	4.2	9.8	11.3
11. 3 g of Turco 5469, 0.2 g of baked epoxy primer and 1 ml of water	4.1	9.8	11.2
	4.2	9.8	11.2
	4.2	9.8	11.2
	4.2	9.8	11.2
12. 3 g of Turco 5469 and 0.2 g of baked polyurethane on epoxy primer	-	9.8	11.3
	4.2	9.8	11.3
	4.2	9.8	11.3
	4.1	9.8	11.3

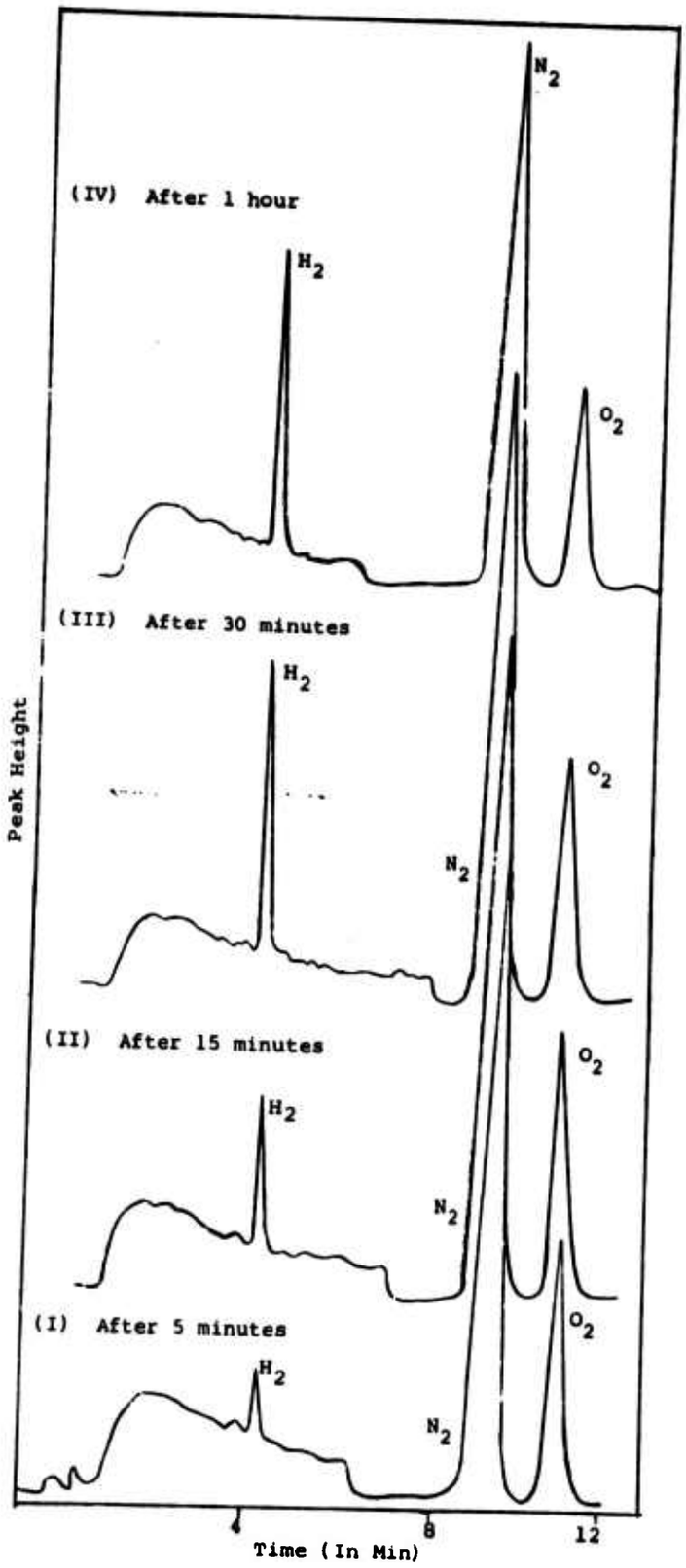


Figure 13

GAS CHROMATOGRAMS OF HYDROGEN IN THE EFFLUENT GASES FROM THE ACTION OF TUFCO-5469 WITH POLYURETHANE FINISHED AIRCRAFT PANEL OVER A PERIOD OF TIME

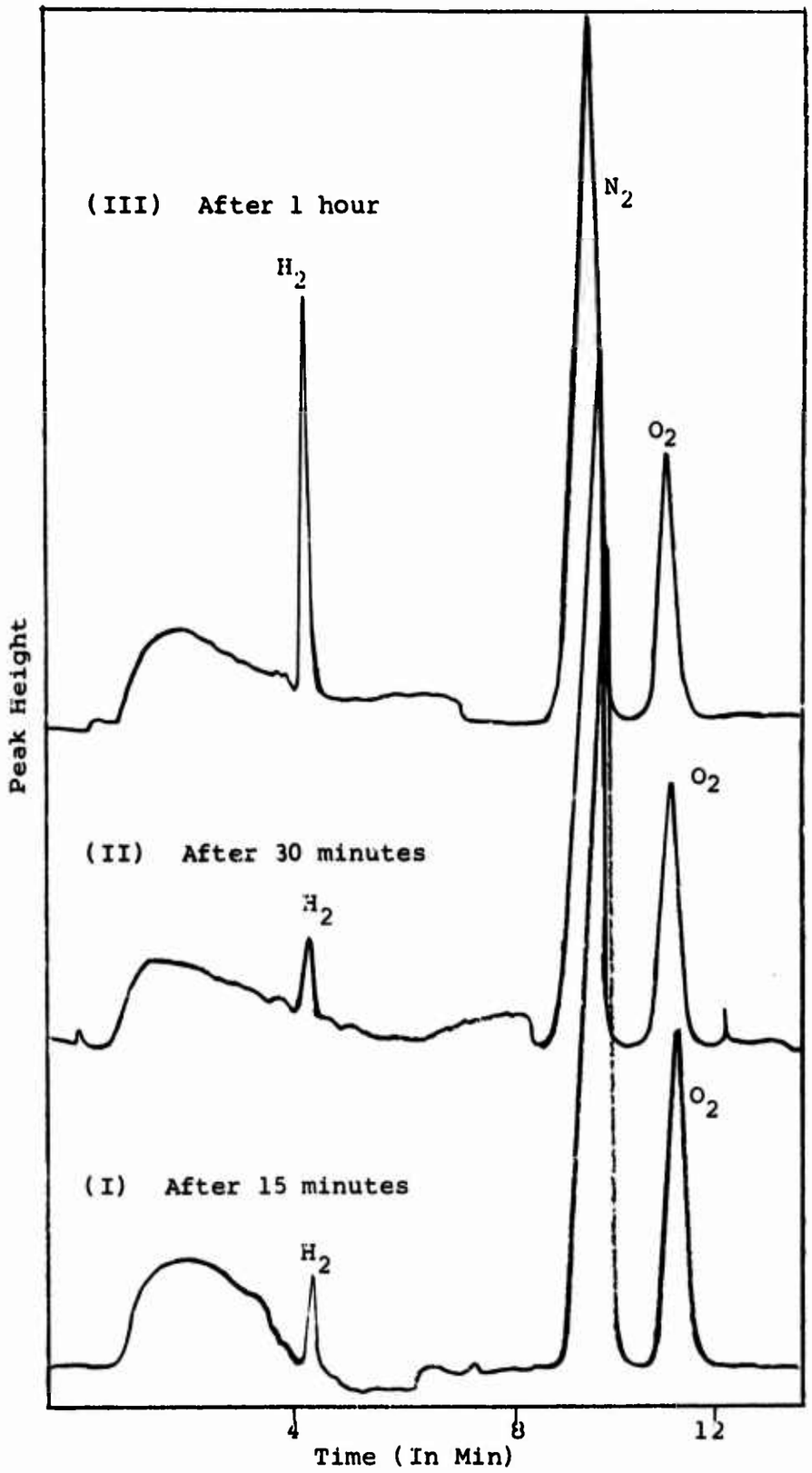


Figure 14

GAS CHROMATOGRAMS OF HYDROGEN IN THE EFFLUENT GASES FROM THE ACTION OF TURCO-5469 WITH SURFACE ACTIVATED, READY-TO-BE PAINTED AIRCRAFT METAL SUBSTRATE OVER A PERIOD OF TIME

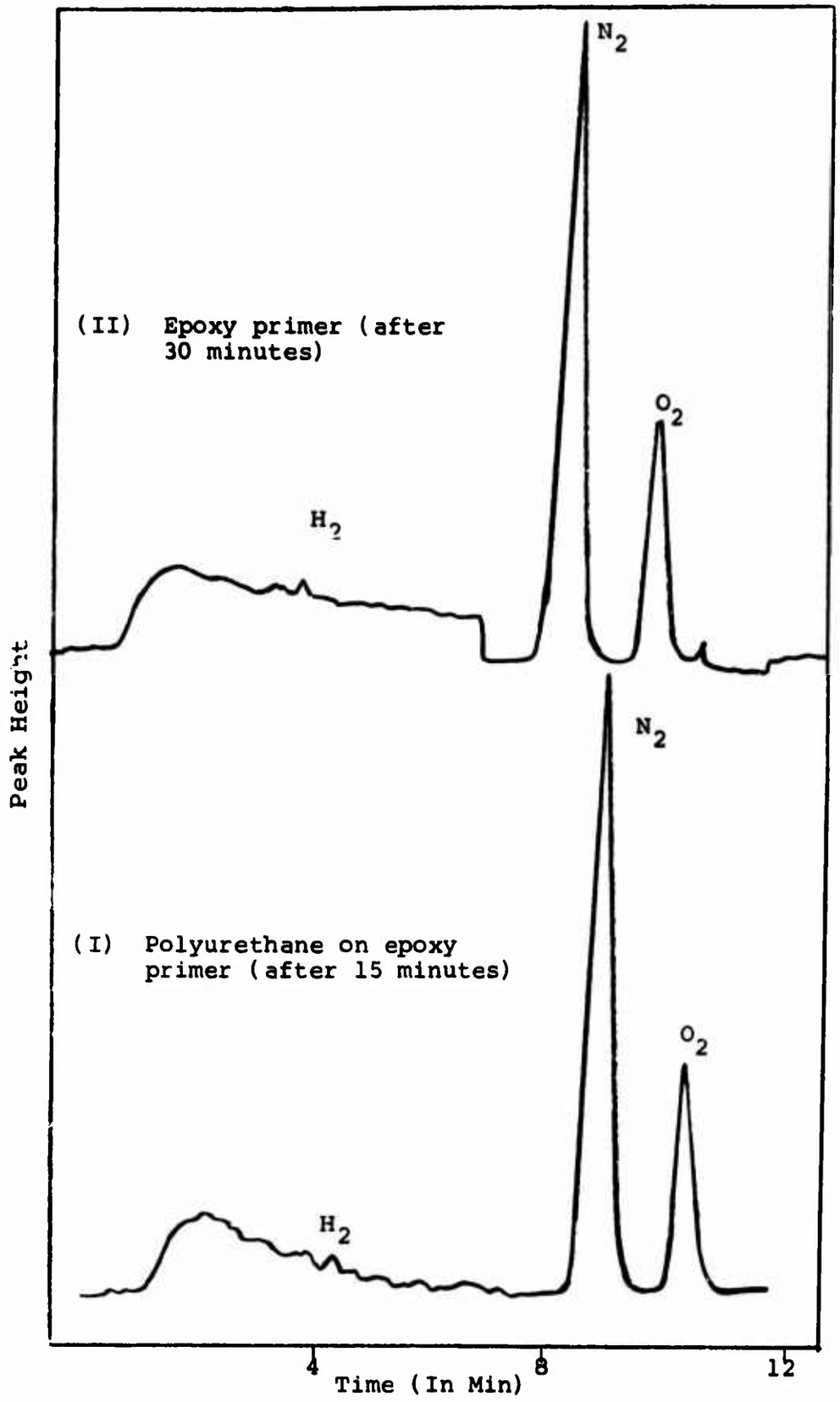


Figure 15

GAS CHROMATOGRAMS OF HYDROGEN IN THE EFFLUENT GASES FROM THE ACTION OF TURCO-5469 WITH THE POLYMER SYSTEMS

coatings. After an initial induction period (which depends on the efficiency of the paint stripper as well as on the nature and history of the paint system), gradual softening of the paint layer occurs followed by swelling of the polymer coating. The swelling of the paint polymer culminates in wrinkling (synonymous with sheeting, folding and crinkling) of the paint film with the concomitant breaking of adhesive bonds between the paint layer and the substrate. The fundamental conditions existing when wrinkling occurs is a swollen gel. When normally insoluble high polymers are placed in contact with an active solvent, the polymer absorbs solvent and expands until an equilibrium condition occurs. In order to accommodate the increased volume and still remain within the original perimeter, the polymer tends to fold or wrinkle so as to relieve internal stresses. This was the explanation offered by Berkeley, Schoenholz and Sheehy[14] for the wrinkling of organic polymer coatings. These authors further postulate that the solvent mixtures solvate the active groups of the polymer and, in so doing, reduce solid-to-solid adhesion. They maintain that the forces built up in the polymer generally, as a result of swelling together with the weakened adhesion, are sufficiently high enough to tear the film loose from the surface. In a later paper on the mechanism of paint stripping, Spring[15] suggested that once a volatile solvent has reached the metal-coating interface, its vapor pressure might assist in lifting

the coating, although lifting was principally due to the relief of strain in the swollen film.

Earlier in the present study, we concluded that mere swelling of paint polymers by organic solvents does not provide enough energy to lift up the paint layer from the metal substrate. By the same token, the effectiveness of paint strippers like Turco-5469 with polyurethane paint systems is not primarily due to the polymer swelling ability of the constituent organic solvents but probably due to the presence of other chemicals which react either with the substrate metal or the paint system to liberate hydrogen gas. In support of this, we cite the ineffectiveness of methylene chloride, a major constituent present in Turco-5469, as a swelling agent for polyurethane paint systems on metal. In summary, the present work on the evolution of hydrogen during paint stripping taken in conjunction with the earlier described work on polymer swelling with organic solvents strongly suggests that the mechanism of paint removal is not solely dependent on the swelling abilities of organic solvents.

D. Chemical Nature of Linear Polyurethane Finished Paint Surfaces

Metals and polymers are not particularly miscible or mutually compatible; experience, however, has shown that bonding between them can be greatly enhanced by metal surface conversions. In the paint systems under consideration,

tenacious bonding between metal and paint polymer is accomplished by the use of an epoxy primer as undercoating besides the surface preparation of the metal itself. In these interface conversions which result in more intimate bonding between paint and metal, chemical reactions play important roles. These reactions could conceivably take place either on the paint surface or interlayers of the paint polymers as well as metal surface and paint polymers.[16] As a prelude to future work on the chemical nature of paint surfaces, we have undertaken the infrared spectroscopic examination of linear polyurethane finished paint systems. To date, work on this aspect of the problem is incomplete. However, the specular reflection spectra* of baked and unbaked polyurethane and polyurethane on epoxy paint polymers as well as the absorption spectra of baked and unbaked epoxy primer are included in the present report more for the sake of completeness than for discussion (Figures 16, 17 and 18).

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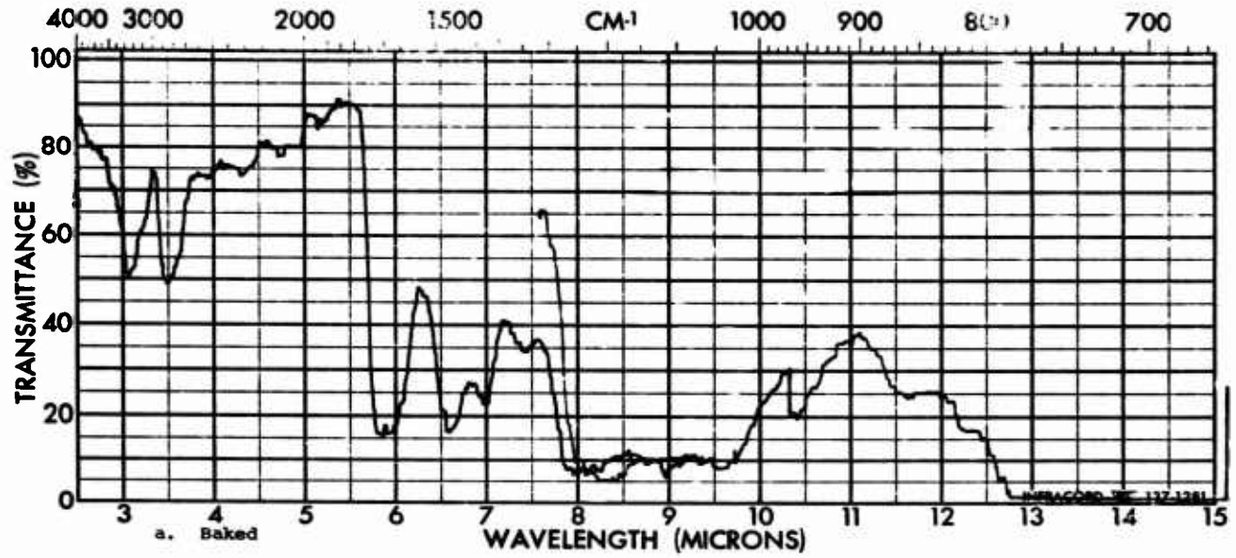
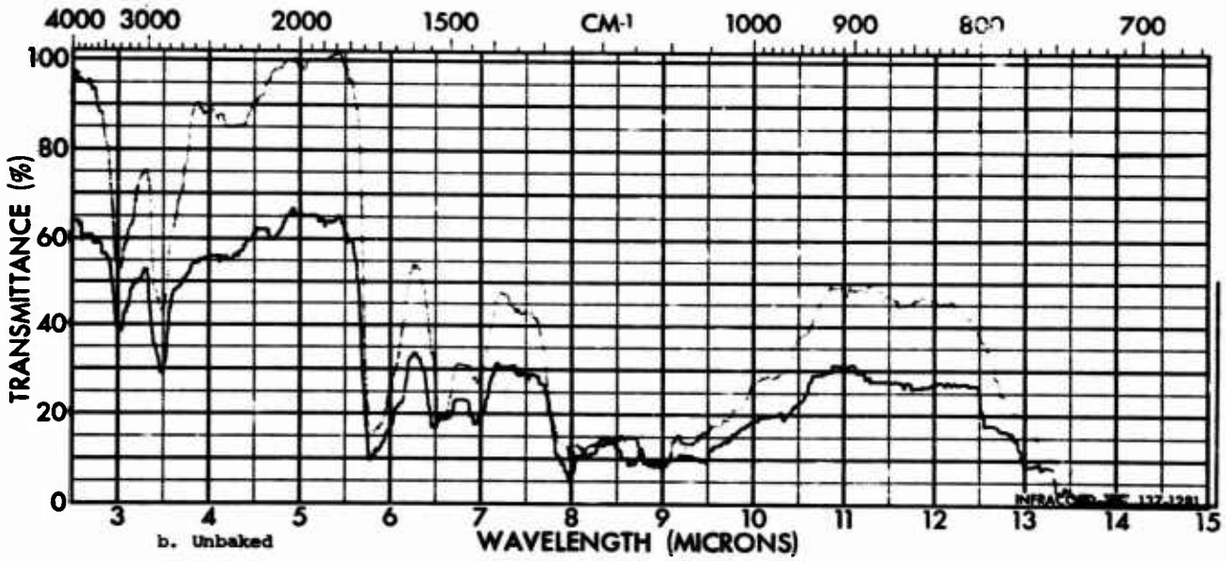
*In order to obtain quantitative information specular reflection is usually recorded as a function of frequency rather than wavelength;[17] however, in this preliminary work it is plotted as a function of wavelength as in the normal infrared absorption spectra.



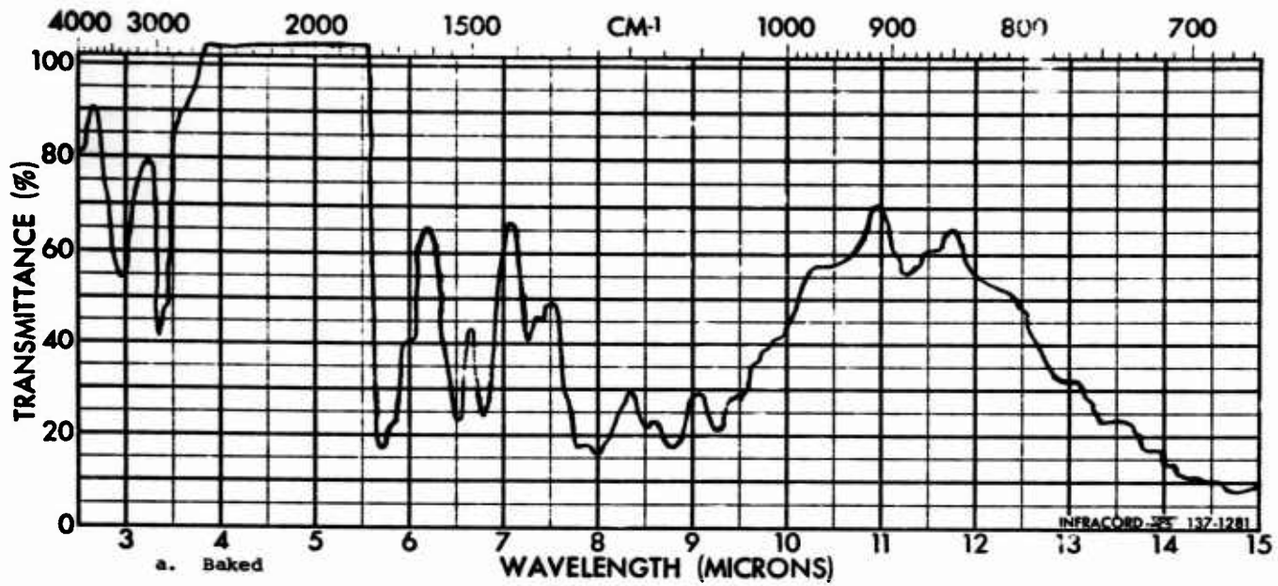
a. Baked



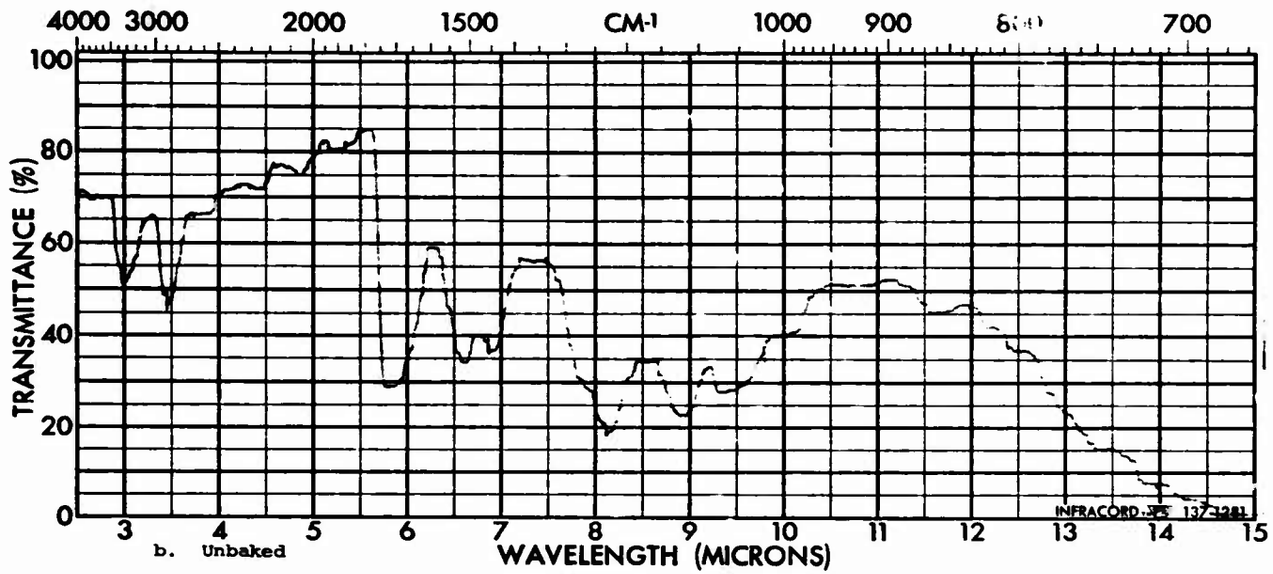
b. Unbaked

Figure 16

SPECULAR INFRARED REFLECTION SPECTRA OF POLYURETHANE PAINT POLYMER
(16a. Baked and 16b. Unbaked)



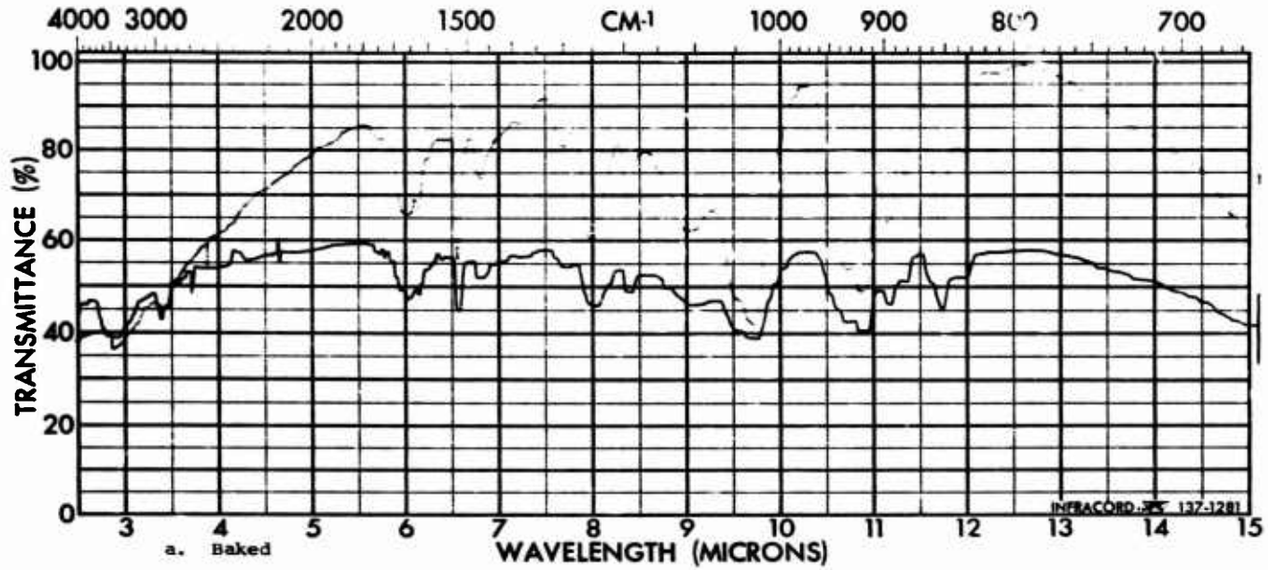
a. Baked



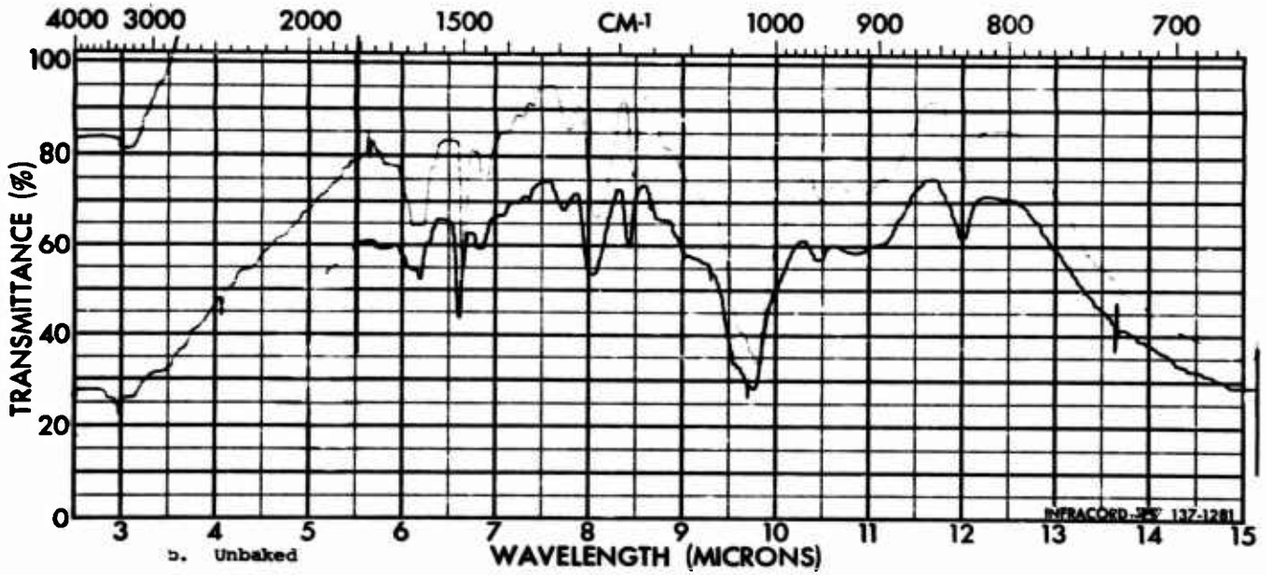
b. Unbaked

Figure 17

SPECULAR INFRARED REFLECTION SPECTRA OF POLYURETHANE ON EPOXY PAINT SYSTEM
(17a. Baked and 17b. Unbaked)



a. Baked



b. Unbaked

Figure 18

INFRARED ABSORPTION SPECTRA OF EPOXY PRIMER COATING
(18a. Baked and 18b. Unbaked)

III. EXPERIMENTAL

A. Swelling of Paint Polymers

1. Test Materials

a. Polyurethane Polymer Paint

Polyurethane aircraft finishes (910-177, Super Desothane Enamel, activator and 821-010, Super Desothane enamel white) were obtained through the courtesy of DeSoto Coatings, Inc. The paint solution was prepared according to the instructions and sprayed onto a glass plate (15 cm x 30 cm, pretreated by washing successively with water, toluene and acetone) using a conventional aerosol spray applicator with a #3 tip. The spraying was carried out under a pressure of 30-40 psi of compressed air. The paint system was allowed to dry overnight at room temperature and then baked 90 hr at 250°F, 10 hr at 300°F, 2 hr at 350°F and half an hour at 400°F. The paint film was lifted up with razor blade from the glass plate in convenient strips. The thickness of the polyurethane film strips, as determined on Model 549 Micrometer (Testing Machines Inc., Mineola, L. I., N. Y.) varied from 0.035 to 0.050 mm.

In another experiment, a polyurethane paint system on metal substrate was obtained in the following way: A mixture of polyurethane aircraft finishes (910-177, Super Desothane Enamel, activator and 821-010, Super Desothane Enamel, white) were prepared according to the instructions and sprayed onto a surface activated, ready-to-be painted aircraft metal panel (12.5 x 40 cm) using a conventional aerosol spray applicator

with a #3 tip. The spraying was carried out under a pressure of 30-40 psi of compressed air. The paint system was allowed to dry overnight at room temperature and then baked 90 hr at 250°F, 10 hr at 300°F, 2 hr at 350°F and half an hour at 400°F. The thickness of the polyurethane paint layer, as determined by Model 549 Micrometer (Testing Machines Inc., Mineola, L. I., N. Y.), was 1.29 mil.

b. Epoxy Primer System

A freshly prepared solution of epoxy primer (MIL-P-23377) was sprayed onto the tin foil (0.5 mm thick) covering a glass plate (15 cm x 30 cm) in the usual manner with an aerosol spray. The epoxy coated substrate (tin foil and the glass plate) was allowed to stand overnight at room temperature and then subjected to the baking cycle as specified in the preparation of the polyurethane film. The tin foil containing the epoxy primer was peeled off the glass plate and placed over mercury in an evaporating dish. Amalgamation of tin foil left behind the epoxy primer film (thickness 1.6 mil) which was used in the swelling measurements.

An epoxy coated aircraft metal panel was prepared in a manner analogous to the polyurethane coated panel.

c. Polyurethane on Epoxy Primer

An epoxy coating on the tin foil covering the glass plate was prepared as usual and allowed to dry overnight at room temperature. The polyurethane paint polymer was then sprayed onto the epoxy primer coating and the paint system was subjected

to the baking cycle. Amalgamation of the tin foil left behind a 3.8 mil thick polyurethane on epoxy film.

The polyurethane on epoxy coating over the aircraft metal substrate was prepared in the usual manner.

2. Preliminary Screening of Solvents

Small strips or bits of polymer paints were placed in test tubes (7 cm x 1 cm) containing different solvents. Indications for swelling or solubility were ascertained by the ease with which the paint scrapings could be dispersed in the solvent when scratched with a glass rod.

3. Swelling Measurements of the Paint Systems with Selected Solvents

A small square of the baked polymer film was placed between a microscope slide and a cover glass. The thickness of the polymer specimen was determined on a Micrometer Model 549 after giving due allowance for the thickness of the cover glass. The microscope slide was placed under a microscope (Spencer's Binocular Model) and the initial length and width of the specimen were measured by means of a millimeter graph paper (K and E graph sheet 46-1513) placed beneath the slide assembly. The solvent was drawn between the slides by capillary action and the movement of the liquid towards the specimen was followed under the microscope. Additional solvent was added whenever needed to compensate for the evaporational losses. The physical changes taking place in the polymer specimen were followed continuously for a total period of thirty minutes. With some solvents, the polymer film merely expanded whereas with others

it folded and buckled. The end of the swelling of the polymer in most of the cases was marked by the flattening of the film. At this point, final readings for the length and width of the swollen polymer were taken. The final measurement for the thickness of the swollen polymer was also made by means of a Micrometer. This measurement is not accurate in view of the solvent trapped between the microscopic slides in spite of the fact that due compensation has been made for the thickness contributed by the solvent (0.003 mm). During these swelling measurements, no particular effort was made to maintain a constant temperature and the experiments were conducted at room temperature (23°C).

In the case of polyurethane over epoxy paint system two types of measurements, one with the epoxy primer as the surface and the other with polyurethane portion as the surface, were taken. The changes in area ($\triangle A$) and volume ($\triangle V$) were calculated in the usual manner.

4. Permeation and Penetration Characteristics of the Solvents

Artificial pinholes were made by an automatic center punch No. 79 instrument (General Hardware Mfg. Co., Inc., New York, N.Y.) on the surfaces of the three paint systems (i.e., epoxy, polyurethane and polyurethane on epoxy primer) over the metal and glass plates as substrates. Droplets of solvents were placed over the pinholes and covered with microscopic cover slides. Additional drops of solvent were added as needed to compensate for the evaporational losses. The changes in the

paint surface polymers were recorded over a period of 24 hr at convenient intervals.

5. Physical Nature of Linear Polyurethane Finished Paint System

Surface photographs were taken with a scanning Electron Microscope (Type JSM-2; manufacturer: JEOLCO) at our Institute.

B. Evolution of Hydrogen Gas During Paint Stripping

Turco-5469, an acid type paint stripper, was supplied through the courtesy of Turco Products, Division of Purex Inc., Chicago, Illinois.

1. Preparation of the Gas Samples

Turco-5469 (3 g) was placed, along with the substrate sample, in a glass vial containing a magnetic stirring bar and the vial was made air tight by means of a rubber septum. The mixture was stirred magnetically and, after an interval of 5 minutes, a gas sample was syringed out and injected into the gas chromatographic column. Further samples for gas chromatography were syringed out at intervals of 15, 30, 45 and 60 minutes.

2. Gas Chromatography

A Varian Aerograph Model 1800 dual column instrument equipped with four filament thermal detectors was used for monitoring the hydrogen in gas samples. A copper column (22' x 1/4") packed with Porapak Q (a polymer composed of ethylvinylbenzene crosslinked with divinylbenzene; 50-80 mesh)

and cooled in a dry ice-trichloroethylene freezing mixture was used for the gas chromatographic analysis. The other column in the instrument was a blank copper column maintained at room temperature. The instrument was operated at the detector temperature of 115° and filament current of 100 ma with argon as carrier gas flow of 30 ml/min. The sensitivity of the instrument for hydrogen at these operating conditions is ca 0.0001%.

C. Chemical Nature of Linear Polyurethane Finished Paint Surfaces

Infrared spectra were recorded on a Perkin Elmer 137 sodium chloride spectrophotometer. The specular reflection spectra were obtained by employing Wilks Model 12 multiple internal reflection (MIR) attachment (supplier: Wilks Scientific Corporation, South Norwalk, Conn.)

IV. SUMMARY AND CONCLUSIONS

In the past a search for suitable organic solvents for inclusion into the paint strippers was usually conducted on a hit or miss basis. Moreover, in most of these investigations paint panels were used to hasten the search and accomplish the task on hand. These down-to-earth approaches, however, resulted in an oversimplification of the parameters involved in the paint stripping process. For example, the wrinkling, which denotes the breaking of bonds between the paint layer and metal, was regarded to be synonymous with the swelling of paint polymers by organic solvents. To explain the lack of action of some organic solvents in causing the swelling of the paint polymer, the questions about penetration and permeation of the paint surfaces by the solvents were raised. When some of these dubious premises formed the basis for the formulation of paint strippers to remove newer and more adhesive paints like polyurethanes, the results were understandably discouraging.

In the course of present work, we developed a rational approach for the selection of solvents for inclusion into new paint strippers. At the beginning, a large number of solvents were examined for the visual evidence of physical changes in laboratory-made paint films. The promising solvents among them were then used in the measurements of their swelling abilities with the laboratory-made paint films by means of the Rapid Swelling Test method. These swelling

measurements resulted in a list of nearly fifteen solvents which are most likely to be successful in paint strippers, provided the swelling of paint polymer is directly proportional to the stripping. These selected solvents had no effect on the test paint panels thereby indicating that polymer swelling is not the main determining parameter in the paint removal. The possible explanation that these solvents did not penetrate the paint layer becomes untenable in view of the presence of pinholes, crevices and other imperfections in the paint surface as revealed by scanning electron microscopy. However, it became evident from the subsequent work with the effective paint strippers (e.g., Turco-5469) that some other parameters, such as liberation of hydrogen gas, influence the stripping of linear polyurethane paint system.

In conclusion, the present work focussed the attention on the need for a better understanding of the mechanism of paint stripping. It is our belief that future work on the study of parameters affecting the interfacial band strength of difficult to remove linear polyurethane aircraft paint systems should be directed towards the fundamental aspects of chemistry and physics of paint surfaces.

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