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The Decomposition of Organic Resins at High Temperature in a Vacuum Environment

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I. INTRODUCTION

There are a great number of uses for organic materials in today's satellites and missiles, and indications are that increased emphasis will be placed upon this class of materials in the space stations and advanced design probes of tomorrow. We believe this statement to be especially true regarding organic coatings and their role in learning more about the universe.

Where organic coatings were once, not too long ago, used solely for corrosion protection and decoration they now appear extremely attractive for their versatile optical properties, combined with ease of application and "tailoring" the optical properties. Where organic coatings were once subject to atmospheric weathering and chemical corrosion they must now be compounded to withstand variable temperatures, combined with high vacuum, and in many cases, intense ultraviolet light.

Accordingly, as the environmental use of these materials change, so must the way in which we study them. Many of the papers being presented at this meeting are indicative of the changed direction of this research area.

The Coatings Section of the Nonmetallic Materials Laboratory, WADD, has undertaken a rather comprehensive study of the organic resins which are used in formulating the finished coating systems to be further "tailored" or blended to accomplish a particular mission. It is anticipated that organic coating resins cured into thin films will be used as the basis for temperature control coatings, binders for dry film lubricant systems,⁽¹⁾ substrates for vapor deposited reflective metals, and a host of other uses at various temperature levels.

Neglecting for the moment nuclear and ultraviolet radiation effects, this study has as its primary subject the degrading affect that vacuum and temperature above the ambient has on these unmodified resins.

II. OBJECTIVES OF THE PROGRAM

The immediate objectives of the present vacuum-thermal program are the following:

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1. To elucidate the useful temperature limits of the numerous classes of presently available film-forming resins in a vacuum environment.
2. To gain an insight as to the chemical mechanism of degradation and the affect of varying chemical structure.
3. To observe the individual and combined affect of film thickness and curing schedules.

III. METHOD AND APPARATUS

The simple technique we have used to gain this type of information has involved the exposure of specimens of known material composition and thickness, cured onto metallic substrates. A vacuum in the range of 10^{-5} mm. mercury and varying temperature levels are used. After a twenty-four hour exposure period the accumulative weight loss and physical changes are recorded.

A bell jar type vacuum system with internal heating chamber and temperature control system was utilized in this work. The temperature is measured by attaching chromel-alumel thermocouples to the front and rear of a duplicate sample panel. The temperature recorded on the front side of the specimen reflects the temperature of the film surface plus the influence of the optical properties of the thermocouple bead itself. The temperature measured on the rear of the sample panel reflects the influence of the absorption-emission properties of the coating on the metal substrate. The mean of these temperatures, which varies from 5 to 20^oF, is the temperature reported.

Heating is accomplished by thermal radiation from a tantalum filament, and is controlled by an external variac. The samples are situated on a steel sample holder which is insulated from the baseplate by glass microscope slides, as is the heating chamber itself. The semi-enclosed heating chamber is covered by a steel bell jar for evacuation.

In this manner, we have been able to gather a large amount of qualitative information which has enabled the definition of the useful upper limits of several classes of resins. Maximum operating temperatures in a vacuum rarely parallels that of an atmospheric exposure.

The effect of exposure on such important physical properties as adhesion and color stability (visible) have been determined. Finally the temperature range of the maximum rate of degradation of a number of cured films has been recorded, thus enabling consideration of a more detailed kinetic study. This study will be described in a latter portion of this report.

IV. RESULTS OF VACUUM-THERMAL EXPOSURES

In order to show what might be expected in attempting to use various classes of resins in a vacuum-thermal environment, it would be of interest to point out some of the results of our exposures concerning, principally, three different classes of organic film-forming resins; certain vinyls, polyurethanes, and silicones. All materials described are commercially available, unmodified, basic resins.* All exposures are made on freshly obtained samples, which will nevertheless contain certain impurities. However, these are the materials being used and which will continue to be so used in formulating finished systems for use in a high vacuum environment.

A. Certain Vinyls

The vinyl resins provide an interesting series of results when one considers weight changes and gross physical effects. Figure 1 shows the results of some of our earlier work with these resins.⁽²⁾ Polyvinyl butyral is an example of a film-forming polymer which undergoes a severe rate of weight loss through all temperature ranges studied. This uniform volatilization of degraded fragments is in sharp contrast with the three other vinyls studied; Kel-F 820, styrene butadiene, and a vinyl co-polymer. The latter materials exhibit promising stability to a point, after which degradation is catastrophic. Co-incident with the bulk degradation and volatilization is a marked change in physical properties as exhibited by severe cracking and crazing.

Therefore, our initial studies in this area served to point out the expected, that organic resins would degrade thermally in vacuo. However, in many cases such degradation took place much sooner and at lower temperatures than did the same material in air. Degradation here is evidently following one or both of two non-oxidative routes; (1) bond cleavage followed by volatilization of the degraded fragments, and, (2) extreme crosslinking by reaction at active sites along the polymer chain leading to embrittlement.

B. The Polyurethanes⁽³⁾

It is therefore of interest to determine what factors have the greatest influence upon the stability of a resin in thin film form. In analyzing the organic coating resin the following variables must be considered:

1. Primary bond type.
2. Method of cure.

* NOTE: None of the materials tested were developed or intended by the manufacturer for the conditions to which they were subjected. Any failure or poor performance is therefore not indicative of the utility of the material under less stringent conditions or for other applications.

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3. Secondary chemical structures present.
4. Film thickness.

In taking these factors into account, the polyurethanes seem to lend themselves well to individual control of these variables. Since these materials are self-catalyzed by the reaction of the isocyanate component and hydroxyl-terminated polyester components, curing could be controlled by humidity in view of the sensitivity of isocyanates to moisture.

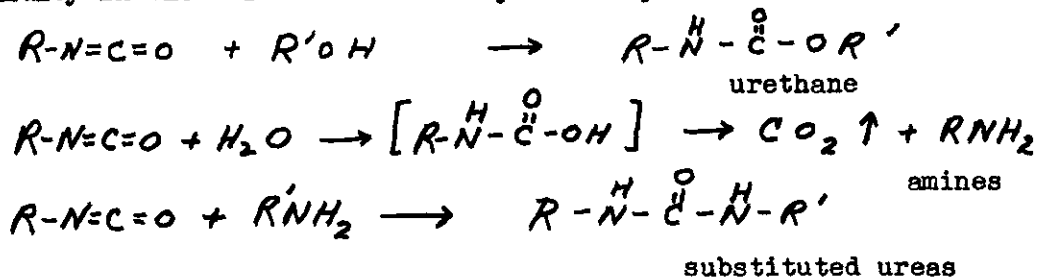


Figure 3. Urethane Forming and Moisture Reactions.

All of the materials studied in Figure 2 are toluene diisocyanate based urethanes. Variation in secondary structure is easily achieved by selecting different polyesters of known degree of branching and functionality. The primary chemical bond in a dry cured film is, of course, the urethane bond (see Figure 3). The inherent thermal instability of this bond is responsible for the gross degradation characteristics of the resins as a class.

Increasing the humidity during cure gives rise to amine groups which on reaction with additional isocyanate yields substituted ureas (see Figure 3). In almost every case studied a dry cure resulted in considerably less weight loss both at the lower temperatures, and in some cases, where degradation is rapid. In all cases, breakdown is essentially complete at 500°F. Degradation is affected only to a relatively minor amount by branching, degree of crosslinking, and film thickness. It may therefore be concluded that the thermal lability to dissociation of the urethane bond is primarily responsible for the observed degradation.

Worthy of mention here is the way in which polyurethanes retain excellent coating properties while undergoing degradation. They do not craze, crack, or char. The only visual evidence of change is one of slight to moderate yellowing. This fact, coupled with desirable room temperature cure characteristics, make the polyurethanes quite suitable for many applications at lower temperatures in a vacuum environment.

C. The Silicones⁽⁴⁾

For higher temperature systems in the atmosphere one naturally thinks of the silicones. To us, then, it was of interest to look at the silicones in the vacuum. This is the area in which we are currently working. It has provided a number of surprises in terms of unanticipated results.

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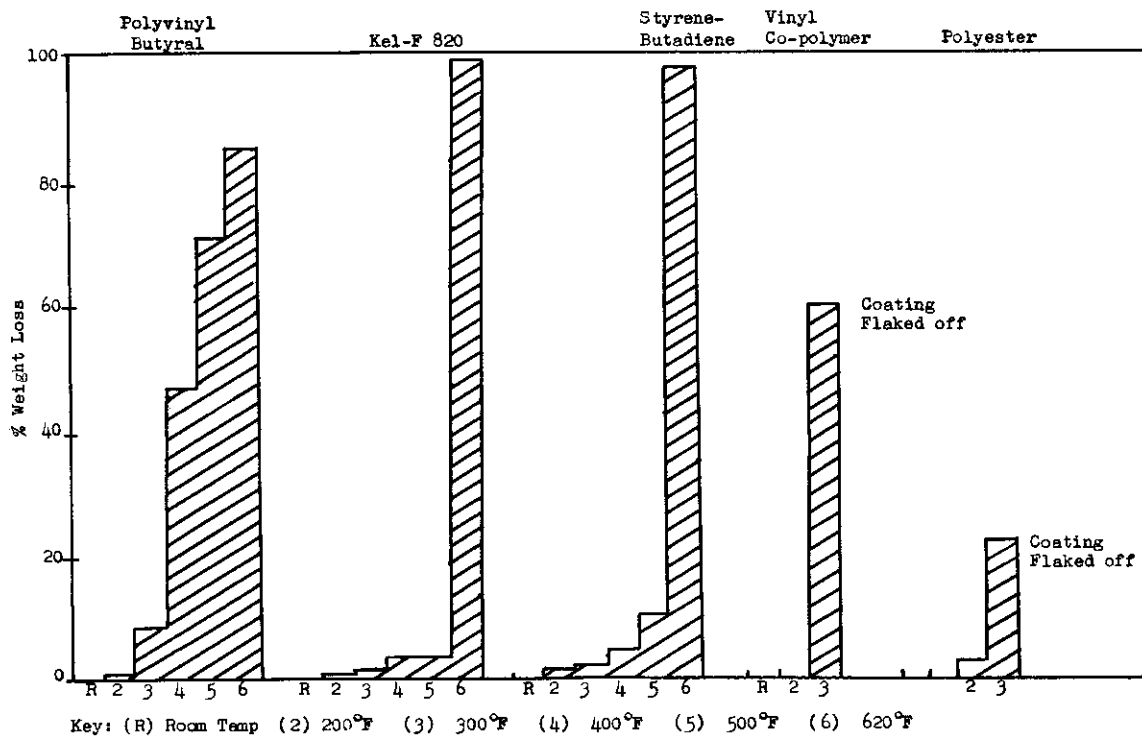


Figure 1 The Vacuum Stability of Vinyl Coatings and a Polyester

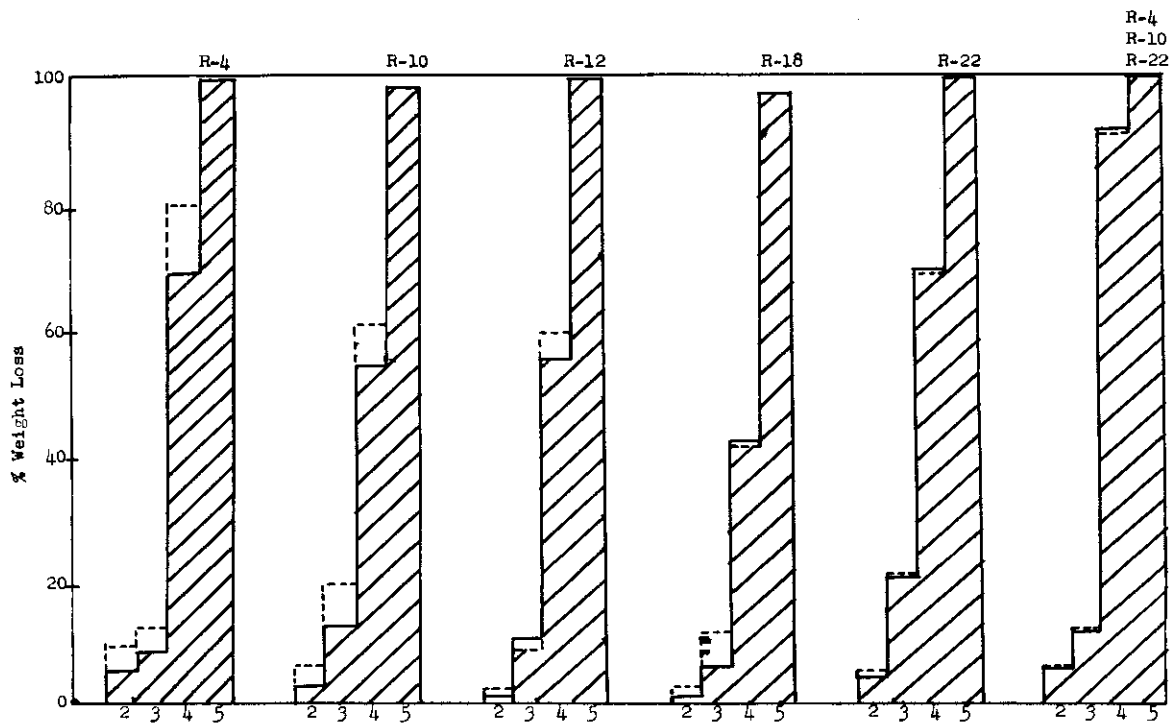


Figure 2 The Vacuum Stability of Polyurethane Coatings

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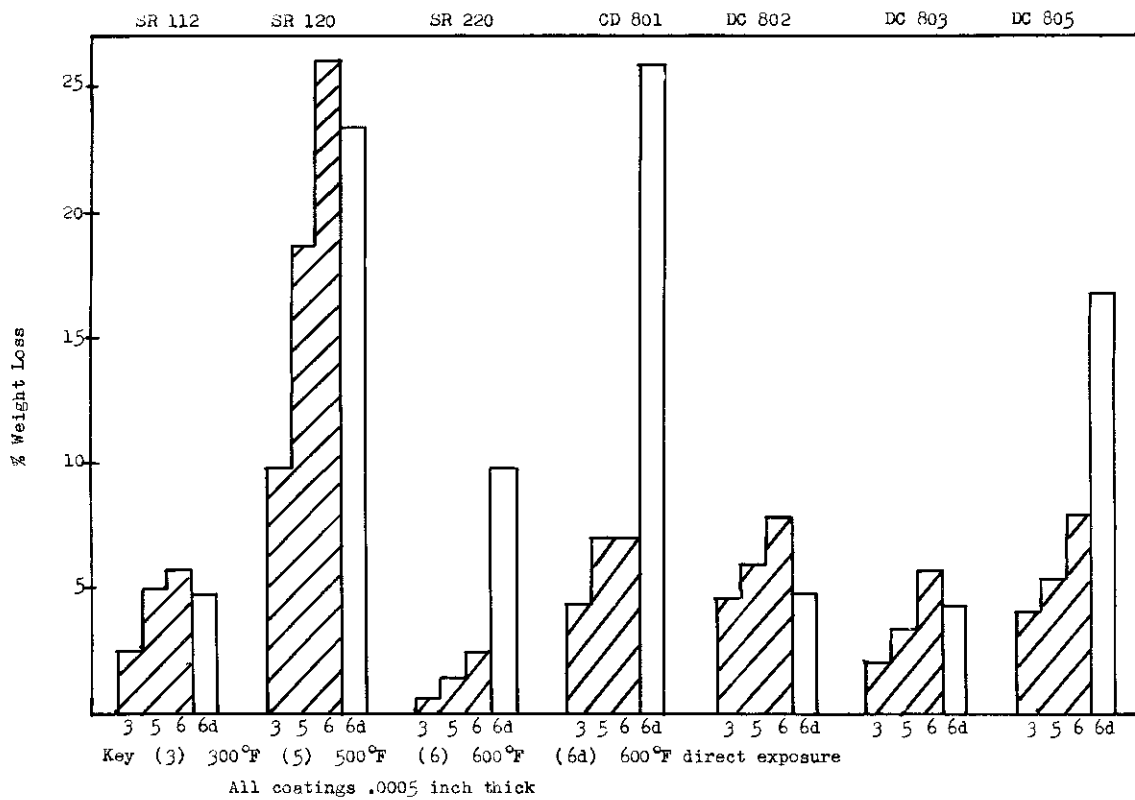


Figure 4 Vacuum Stability of Silicone Coatings

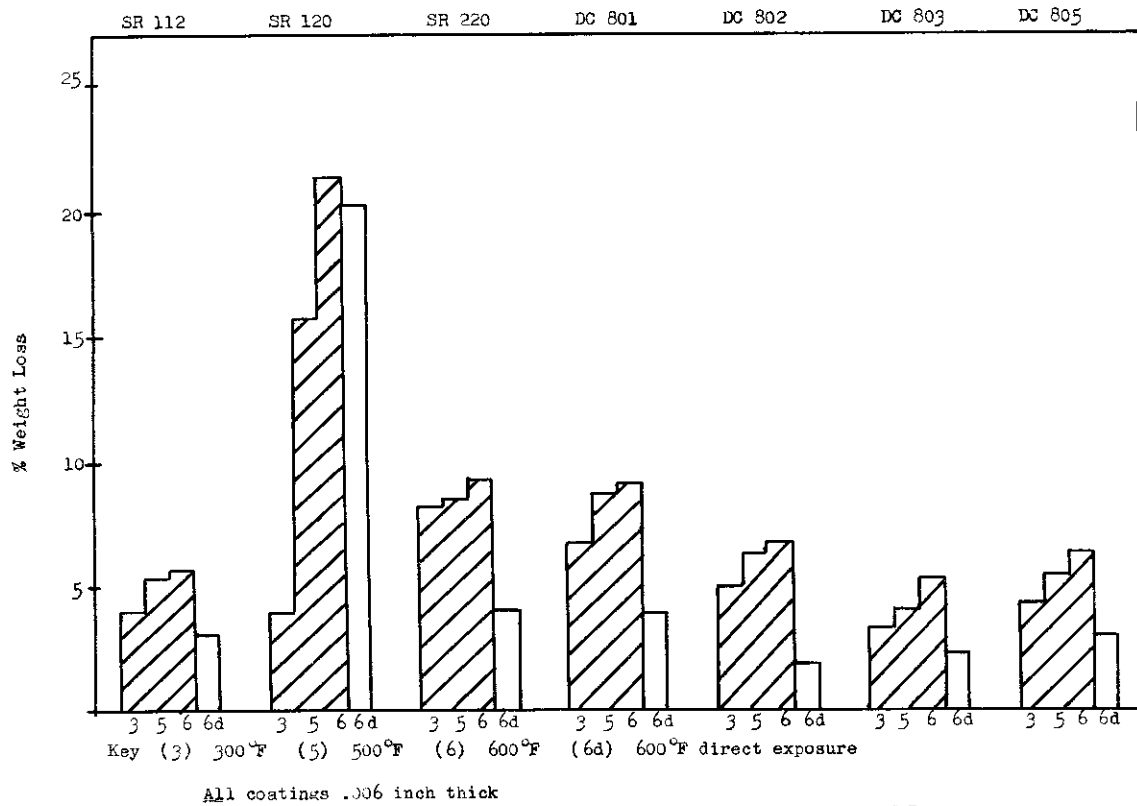


Figure 5 Vacuum Stability of Silicone Coatings

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For example, some typical silicones were cured 4 hours, at 500°F in air and exposed 24 hours in the vacuum at the same temperature. Drastic changes were noted with these resins, although weight loss was slight. Breakdown was manifested chiefly by cracking and loss of adhesion. These observations give cause for grave concern over the use of many commonly available silicone resins as coating materials in the vacuum environment at comparatively low temperatures.

When one analyzes the possible degradation processes, these results, though surprising, are not too extraordinary. In air at 500°F slight oxidation of side groups occurs at extended exposure. In vacuum, cyclization is known to occur, and any degradation is thermal in nature. In addition, further dehydration and crosslinking contributes to the embrittlement of the film. In many cases we observed complete shattering of the film and loss of adhesion of unmodified silicone resins.

In our current work, concerned with some twenty different silicone resins, the observed phenomena are being studied as a function of curing time in air, curing temperature and the degree of methylation or phenylation of the system.

As far as weight loss is concerned, the commercially available silicone resins exhibit less deterioration than any other class studied. Figures 4 & 5 show the magnitude of weight loss of some representative materials. The figures also point out how step-wise weight loss to 600°F differs from a direct exposure to this temperature level in vacuum, and how film thickness affects both types of exposure. Direct exposure to a high temperature often results in more serious weight losses in thinner films. On the other hand, thicker films usually exhibit considerably less weight loss at least to 600°F.

V. FUTURE PROGRAMS

The study of unmodified organic coating resins in the manner described is considered to be about 50 percent complete. A consideration of the epoxy resins and such nitrogen containing polymers as the melamines and polyamides will complete this phase of the work.

As useful as this type of information might be, it must be conceded that it is of a qualitative nature, especially since weight loss measurements had to be made after the sample was cooled and exposed again to air.

The apparatus shown in Figure 6 is presently being set up in our Laboratory and will make available quantitative data with which we hope to analyze the kinetics of polymer film degradation while the material undergoes vacuum pyrolysis. These films will be studied on a metallic substrate and subject to the added stresses accompanying thin coatings on metal. The method to be used is one of continuous weight loss. Measurements will be made at constant and varying temperature levels.



Fig. 6 Continuous Weight Loss Vacuum Balance and Recorder

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From this type of study we hope to obtain the following important types of information:

1. The energy of activation and kinetic order of the degradation reaction of a wide variety of organic coating resins.
2. A better insight as to the different modes of degradation, as well as the degree of breakdown, in the bulk, powdered, and thin film states.
3. What effect an added flux of ultraviolet radiation will have on these resins at comparatively high temperatures.

VI. SUMMARY

In concluding, some important facets should be taken into account when the use of organic coatings in a vacuum-thermal environment is desired.

First, the basic chemical structure must be considered since this will dictate, to a large measure, the useful upper limits of finished systems. For example, polyurethanes, at least those based upon toluene diisocyanate and polyesters, will probably be of little use above 350°F. This is true of many other resins, such as straight polyesters and silicone alkyds, which contain ester linkages.

Second, it has been our experience that weight loss alone must not be used as the sole criterion for the stability of a system. A material may undergo drastic change in physical and optical properties with only insignificant changes in weight. The silicones, which undoubtedly will be candidates for the higher temperature applications, are a case in point.

Third, optimum curing conditions will have to be selected in order to achieve maximum temperature resistance. Such curing schedules may well vary from those giving optimum properties in the atmosphere.

Finally, for higher temperature systems to be exposed to direct solar intensities, one must consider the combined effects of vacuum, temperature, and ultraviolet light.

Within the coming year we hope to obtain the answers to some of these practical questions, while simultaneously learning enough about the fundamental processes of thin film degradation so that higher temperature and more stable materials might be made available.

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