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FINAL REPORT

DEVELOPMENT OF PHASE-CHANGE COATINGS  
FOR USE AS VARIABLE THERMAL CONTROL SURFACES

By R. N. Griffin and B. Linder

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Prepared under Contract NAS1-6166 by

Materials Sciences Section  
Space Sciences Laboratory  
Missile and Space Division  
General Electric Company  
P. O. Box 8555  
Philadelphia, Pa. 19101

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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## FOREWORD

This document "Development of Phase-Change Coatings for Use as Variable Thermal Control Surfaces" is the final report on the program conducted during the period of March 8, 1967, to March 8, 1968 for the National Aeronautics and Space Administration under Contract NAS1-6166. The program was monitored by Mr. Warren Kelliher of the Langley Research Center of that agency. Dr. R.N. Griffin of the Space Sciences Laboratory, General Electric Missile and Space Division, was the principal investigator.

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DEVELOPMENT OF PHASE-CHANGE COATINGS  
FOR USE AS VARIABLE THERMAL CONTROL SURFACES

By. R. N. Griffin and B. Linder  
General Electric Space Sciences Laboratory

SUMMARY

Phase-change coatings were first developed and demonstrated by the Spacecraft Materials Section at NASA, Langley Research Center. When such coatings are in the transparent state, the pigment and binder are mutually soluble, forming a homogeneous single phase solution. As the temperature is lowered, the saturation temperature for the particular composition of binder and pigment is reached and a portion of the pigment comes out of solution to form a separate phase. However, since this saturation temperature is at or below the melting point of the pigment, crystals of solid pigment are formed dispersed throughout the binder. Thus, when the phase-change coating is in the diffuse state, it is a heterogeneous dispersion of crystalline particles of pigment in amorphous binder.

The further development of phase-change coatings for practical application to spacecraft was begun under Contract NAS1-5330. In that work a phase-change coating system was developed which can be applied by brushing or spraying. It has approximately a two-fold change in absorptance between 25° and 50° C, is stable to 10<sup>3</sup> thermal cycles in vacuum, and is essentially unaffected by exposure in vacuum to 100° C, 1000 equivalent sun-hours of ultraviolet, and 100 Mrad x-radiation<sup>(1)</sup>.

The present work was performed under Contract NAS1-6166 and was devoted primarily to the development of practical phase-change coatings whose operating temperature is as close as possible to normal room temperature. About a hundred formulations were made and tested in the search for a room temperature phase-change coating. At least two room temperature phase-change coatings were developed which may be satisfactory for short missions, but further work is required for the development of such coatings for prolonged exposure in space.

Coatings of dilauryl phosphite in poly(vinyl butyral) undergo a phase-change between about 6° C and 20° C. However, we were unable to find an overcoat which was impermeable to the dilauryl phosphite. As a result, gradual evaporation of the pigment occurred in vacuum.

Formulations of amyl stearate in poly(vinyl butyral) performed well in all respects except that irradiation testing produced variable and inconsistent results. Some samples survived irradiation testing with little damage while in others the overcoat became white and opaque. The use of some other overcoat may suffice to make phase-change coatings containing amyl stearate useful near room temperature.

## I. INTRODUCTION

The ability to control the temperature of a space vehicle with a minimum of weight and maximum reliability has been a goal of thermal design and materials engineers since the advent of the space program. Solutions to this problem have been sought with active thermal control systems which use shutters that open or close depending on the vehicle temperature and with passive control systems which rely on an accurate prediction of radiative properties backed with thermostats and heaters as required.

Both approaches have worked moderately well in meeting the temperature control requirements but both have disadvantages. The active system provides precise control but is relatively complex and heavy. The passive system, while light in weight, provides no protection should overheating occur. A simple and apparently practical "self-thermostatic" thermal control system was first demonstrated at NASA/Langley Research Center. This system is now called a "phase-change coating". The temperature is controlled in much the same way as in the shutter system - by changing the amount of solar energy absorbed in response to changes in the vehicle's skin temperature. Phase-change coatings, however, require no moving parts and are applied as easily as a conventional thermal control coating.

Phase-change coatings operate as self-thermostatic surfaces by exhibiting a reversible change in solar absorptance with temperature. Changes in the absorptance of such coatings are caused by temperature-dependent solubility of the pigment or inclusion material in a transparent binder. In the low temperature state, two phases are present. The difference between the refractive indices of these two phases causes internal scattering and absorption of the sun's energy. In the elevated temperature state the pigment is dissolved in the binder, providing a clear, homogeneous film. Behind this film is a highly reflective surface, exposure of which reduces the heat load on the vehicle.

The objective of the present contractual work was to develop phase-change coating systems which are stable to the vacuum, the ultraviolet radiation, and the high energy radiation generally associated with the space environment. The coatings were to have the physical, mechanical, and optical characteristics requisite for practical application to the spacecraft. Emphasis was placed on surveying different formulations of vehicles and pigments in order to obtain phase-change coatings having the following properties:

- a. Phase-change temperature between  $10^{\circ}\text{C}$  and  $50^{\circ}\text{C}$  with primary emphasis on developing coatings having phase-change temperatures near  $25^{\circ}\text{C}$ .

- b. Fast recovery of crystalline state from transparent state (1 minute or less for an instantaneous  $20^{\circ}\text{C}$  change)
- c. Change in  $\alpha/\epsilon$  ratio by at least a factor of two
- d. Changes in  $\alpha/\epsilon$  ratio reproducible for at least  $10^3$  thermal cycles ( $<5\%$  change)
- e. Stability of optical properties in space environment [ $<5\%$  change in vacuum ( $10^{-6}$  mm Hg) from thermal ( $100^{\circ}\text{C}$ ), U.V. (1,000 sun-hours), and ionizing radiation (100 Mr)] .
- f. Suitable mechanical and physical properties for application to spacecraft surfaces (adhesion, ductility, homogeneity, etc.).

## II. LIST OF SYMBOLS

$\alpha$	solar absorptance
$\epsilon$	emittance
DLP	dilauryl phosphite
TLTTP	trilauryl trithiophosphite
phr	parts by weight per hundred parts resin
ESH	equivalent sun hours
Butvar B98	} types of poly(vinyl butyral)
Butvar B76	
PVB	poly(vinyl butyral)
mp	melting point
fp	freezing point
MW	molecular weight
$n_D^{25}$	refractive index at 25°C and 589 m $\mu$



### III. EXPERIMENTAL

#### A. BINDERS

Because of our earlier success in using poly(vinyl butyral) as the binder in phase-change coatings, prepared under Contract NAS1-5330, the principal effort in this work was devoted to formulations made with this binder.

In addition, we investigated the use of poly(vinyl formal) as a binder either alone or in mixtures with poly(vinyl butyral). Unfortunately, poly(vinyl formal) is a poor film-former, and coatings made from this material were brittle and tended to be yellow. Mixtures of poly(vinyl butyral) and poly(vinyl formal) were not suitable as coatings since the two are immiscible in all proportions from 10:1 butyral:formal to 1:1 butyral:formal. Homogeneous mixtures were obtained in the range of 5:1 to 10:1 formal:butyral, but these binders would not adhere to a metal substrate.

A silicone elastomer (92-009) appeared to have properties desirable for a phase-change coating. Investigation showed, however, that this so-called clear resin is translucent but not transparent, and no further work was done with it.

A few formulations were attempted with RTV 602 as a binder, but none of these attempts met with any marked success.

#### B. PIGMENTS

The criteria for selection of potential phase-change pigments were developed in our earlier work. The selection of pigments was based on melting point, solubility, molecular weight, vapor pressure, and thermal, ultraviolet and radiation stability.

To be considered for possible use as a pigment in this work, a material must melt near room temperature, it must freeze to a crystalline form, must have high molecular weight, must have no reactive functional groups, must be non-hygroscopic, and must have a refractive index significantly different from that of the potential binder. Finally, of course, the material should be available commercially or through relatively straightforward synthesis.

The materials listed in Table I were selected as potential pigments based on the above criteria. In most cases, information on all the criteria was not available, and materials were considered candidates as long as none of the available data indicated they were unsuitable--no matter how many of the other properties were unknown.

TABLE I  
PIGMENT SELECTIONS

<u>Material</u>	<u>m. p., °C</u>	<u><math>n_D^{25}</math></u>
Tridodecylamine	17	1.4558
Propyl sulfone	26.5-27	
Triethanolamine	20	1.4835
Methyl <u>p</u> -toluenesulfonate	27	
2-Tridecanone	28	
<u>n</u> -Tridecylamine	27	
Methyl <u>p</u> -toluate	33	
Dilauryl phosphite	25	1.4487
Trilauryl trithiophosphite	26.8-27	1.5014
Amyl stearate	29-30	
Octadecyl acetate	29-30	
Didecyl sebacate	25-27	

Extensive purification of some of the potential pigments was undertaken, but only after initial formulation screening indicated that the pigments had some potential for success. Purification procedures normally included fractional crystallization, molecular distillation, and zone-refining. Molecular distillations were performed in a rotating film still at pressures down to  $10^{-3}$  torr. Zone-refining was performed with a multiple zone refiner. Interzone cooling was provided by recirculated chilled ethylene glycol/water mixture. The details of purification of some pigments are described in the following paragraphs.

1. Dilauryl Phosphite (DLP)

As received from the manufacturer, DLP was a liquid at room temperature. This material was kept for 24 hours in a water bath at 23°C, whereupon the solid and liquid phases were separated by filtration. The water bath temperature was lowered to 21°C, and the remaining liquid DLP was

fractionally crystallized at this temperature. After two crops of crystals were collected at 21°C, the liquid residue was molecularly distilled twice with inconclusive results. Column chromatography of one still fraction over alumina and over charcoal indicated the presence of seven or eight constituents, a major one of which had the properties of an imino carbonate. On the advice of the manufacturer, we attempted to wash the DLP with 1% sodium hydroxide solution. A stable emulsion was formed which was broken by saturation of the aqueous phase with sodium chloride. No particular improvement in the DLP was noted as a result of this treatment. Finally, the DLP was recrystallized from six times its weight of petroleum ether. Several crystalline fractions were isolated and characterized. Their properties are summarized in Table II. No further attempt was made to identify the impurities or the constituents of the several fractions. Fractions 33A and 33D were used in the formulation studies.

TABLE II  
PHYSICAL PROPERTIES OF FRACTIONS ISOLATED FROM  
DILAURYL PHOSPHITE

<u>Fraction</u>	<u>m. p.</u> <u>(°C)</u>	<u>f. p.</u> <u>(°C)</u>	<u>MW</u>	<u>n<sub>D</sub><sup>25</sup></u>
33A	21			1.4482
33B	21-22			1.4490
33D	25	23	408	1.4487
33E	21		411	1.4479
33G				1.4430
33H				1.4402

2. Trilauryl Trithiophosphate (TLTTP)

The TLTTP as received was part solid, part liquid at room temperature. The whole mass was melted to remove it from the bottle. It was then allowed to stand at room temperature until it had partially recrystallized. The solid and liquid phases were separated by vacuum filtration. The liquid had a molecular weight of 471, as determined by osmometry, and  $n_D^{25}$  1.4946. The solid had a measured molecular weight of 561 and  $n_D^{25}$  1.4987. Washing of the solid with methanol resulted in a measured molecular weight of 610 (theoretical 634) and  $n_D^{25}$  1.5021. When zone-refined, this material melted at 26.8-27.0°C and had  $n_D^{25}$  1.5008.

3. Tridodecylamine

Molecular distillation was carried out at 175°C with mechanical pump vacuum. The distillate had  $n_D^{25}$  1.4558. A second fraction distilled at 190-195°C at about  $10^{-4}$  torr had the same index of refraction, and the residue had almost the same index. Obviously, the molecular distillation was effecting little purification.

4. Propyl Sulfone

This material was partially solidified at room temperature and was filtered under vacuum. The filtrate was washed with methanol and dried under vacuum. The product melted at 26.5-27°C and was apparently unchanged by zone-refining.

5. Triethanolamine

Neither molecular distillation nor attempted fractional crystallization resulted in any measurable change in the properties of the material as received.

6. n-Amyl Stearate

This pigment was synthesized from n-amyl alcohol and stearic acid. Low-boiling impurities were removed from the reaction mixture at 50°C under water aspirator vacuum. Molecular distillation removed additional low-boilers, and finally produced a waxy, slightly yellow solid having a measured molecular weight of 331 (theoretical: 354.6). This material was recrystallized from petroleum ether to give a white product which melted at 29-30°C. Zone-refining of this material resulted in little obvious change in physical properties except for removal of a weak band at  $1800\text{ cm}^{-1}$  in the infrared spectrum as shown in Figure 1. This band was attributed to monomer acid. As is discussed in Section E2, however, zone-refining made a great deal of difference in the behavior of amyl stearate as a phase-change pigment.

7. n-Tridecylamine

All attempts to purify this material by crystallization were unsuccessful. It remained a low-melting glassy substance which could not be zone-refined because its melting point was lower than the lowest refrigerant temperature we were able to maintain. Elemental analysis of the material showed 82.10%C, 14.43%H, and 4.05%N. Osmometry gave a molecular weight of 433. A Hinsberg test gave negative results, and no N-H vibration was evident in the infrared spectrum. Therefore, we believe that this compound was tri-n-decylamine rather than n-tridecylamine. By the time this became evident, we had found several other amines to be unsatisfactory as phase-change pigments, and further investigations with n-tridecylamine did not seem warranted.

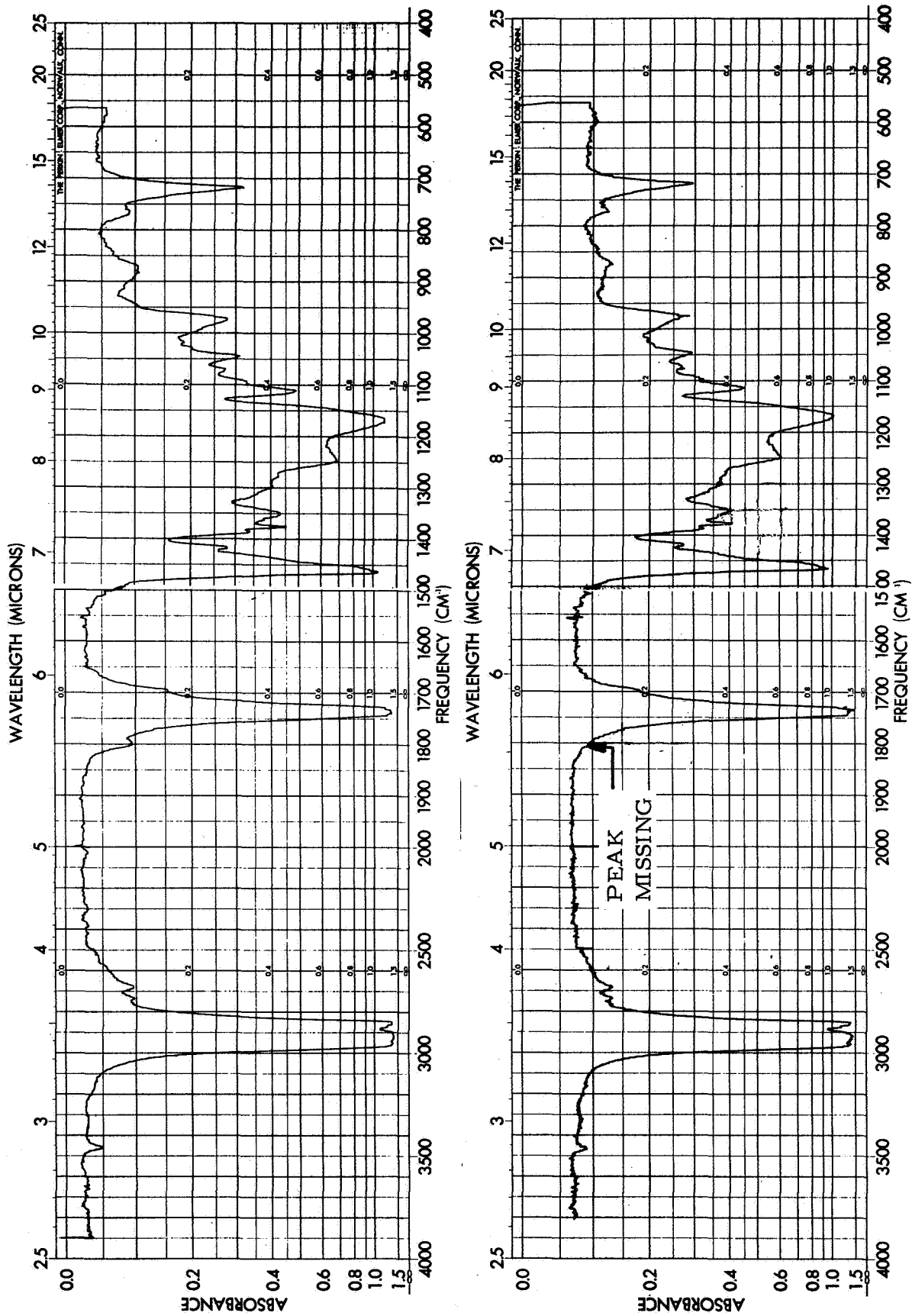


Figure 1. Infrared spectra of amyl stearate before (top) and after (bottom) zone refining

## C. COATING FORMULATIONS

About a hundred coating formulations were made in the course of attempts to make a room-temperature phase-change coating. Data relating to all these formulations are tabulated in Appendix I. More complete descriptions of three of them are given below. In formulations with poly(vinyl butyral) binders, the most convenient solvent was found to be 60% isopropanol, 40% xylene.

### 1. Dilauryl Phosphite (DLP) in Poly(vinyl butyral)

After the dilauryl phosphite had been purified as described above, formulations were made up of dilauryl phosphite and Resoflex R-296 in poly(vinyl butyral) (Butvar B98). At a pigment concentration of 25 phr, the coating remained transparent after prolonged refrigeration at  $-10^{\circ}\text{C}$ . When the concentration of DLP was raised to 50 phr and Resoflex was maintained at 20 phr, a slow phase-change was observed at  $-10^{\circ}\text{C}$ . The performance of the coating was markedly improved by removal of the Resoflex from the formulation. A coating consisting of 50 phr of DLP in Butvar B98 underwent a phase-change at  $-10^{\circ}\text{C}$  and remained opaque at  $+6^{\circ}\text{C}$ . The coating returned to its transparent state between  $6^{\circ}\text{C}$  and  $25^{\circ}\text{C}$ . A similar coating containing 100 phr of pigment behaved in similar fashion except that the phase-change was reversible between room temperature and  $6^{\circ}\text{C}$ . The first indication of serious trouble with this coating was the discovery that a sample overcoated with silicone 391-15-179 became transparent after 250 thermal cycles in vacuum. A small amount of pigment was found on top of the silicone layer. In another case, the silicone overcoat cracked after oven curing. RTV 602 proved unsatisfactory as an overcoat when the pigment was found to come to the surface of the silicone during cure. The use of overcoats of poly(vinyl butyral) cross-linked with hexamethoxymethylmelamine and with tolylene diisocyanate was attempted although it had previously been shown that such a material could actually be used as a binder for a phase-change coating with DLP. In other words, it had been shown that DLP is appreciably soluble in cross-linked poly(vinyl butyral). The results obtained with such an overcoat were not significantly different from those obtained with silicone overcoats. Finally, since we had good reason to believe that this coating would perform satisfactorily with the proper overcoat, attempts were made to laminate it with aluminum foil and poly(vinylidene fluoride). (The chemical similarity between this coating and an earlier successful one<sup>(1)</sup> was the basis for optimism.) Usable laminates were not obtained, however, and the attempt was abandoned.

### 2. Trilauryl Trithiophosphite (TLTTP) in Poly(vinyl butyral)

The optimum formulation appears to be about 12.5 phr of TLTTP in Butvar B98. Such a formulation undergoes a reversible phase change between

6°C and about 28°C, and when overcoated with poly(vinyl butyral) cross-linked with hexamethoxymethylmelamine, this coating can be thermally cycled  $10^3$  times in vacuum without apparent damage. Silicone overcoats may be equally as effective, but silicones generally proved difficult to cure in the presence of TLTP. In an effort to improve the recovery rate of TLTP coatings, a small amount of finely divided silica (Novacite) was added to one formulation. No improvement was noted. The addition of about 0.1 phr of finely ground zeolite (Molecular Sieve 5A), however, resulted in rapid and reversible phase-changes. When such coatings were exposed in vacuum to  $10^3$  equivalent sun-hours of ultraviolet and  $10^8$  rads of x-ray, increases in solar absorptance were observed. In its transparent state, one such coating increased in solar absorptance from 0.13 to 0.20. Because of the pattern of degradation of the sample, we believed that the damage was caused by ultraviolet light rather than x-rays. (The sample appeared undamaged where it was sheltered from light but not from x-rays.) Therefore, 2% of hexamethyl phosphoric triamide was added to the formulation as an ultraviolet screen. The first such sample turned brown and bubbled on irradiation. A second sample was therefore allowed to stand for three weeks before irradiation to minimize residual volatiles. With this sample, however, outgassing was so extensive as to prevent our starting the ion pump on the irradiation system-even after 24 hours of rough pumping. A third sample of the same formulation was irradiated, but because of excessive outgassing a cobalt sulfate filter was used to minimize the visible and infrared light incident on the sample. The amount of cobalt sulfate was gradually reduced and was eventually replaced by the water filter normally used. After less than 220 ESH, the system was opened. The coating sample was brown and distorted.

### 3. Amyl Stearate (AS) in Poly(vinyl butyral)

The most successful formulation was made up of 16 phr of zone-refined amyl stearate, 1 phr of stearic acid, and 10 phr of Resoflex R-296 in poly(vinyl butyral) (Butvar B76). Overcoats of silicone 391-15-170 or of poly(vinyl butyral) cross-linked with hexamethoxymethylmelamine were used to inhibit evaporation of the pigment. This formulation underwent a rapid and reversible phase-change between 6°C and 30°C. A factor of two change in absorptance was recorded, and little or no alteration in properties was observed after  $10^3$  thermal cycles in vacuum. Not all samples of this formulation were equally successful. In some cases an abnormally high absorptance was found, so that even with a good phase-change only a small percentage change in absorptance was observed. An example of a poor sample is shown in Figure 2. Judging from the shape of the curves we believe that the problem lies in the silver substrate rather than in the coating. The shape of the curves in Figure 2 is similar to the shape of reflectance curves of aluminum rather than silver as can be seen from Figure 3. Therefore, we believe that the high absorptance of coatings such as that shown in Figure 2 does not represent a major coatings problem but rather some problem in the

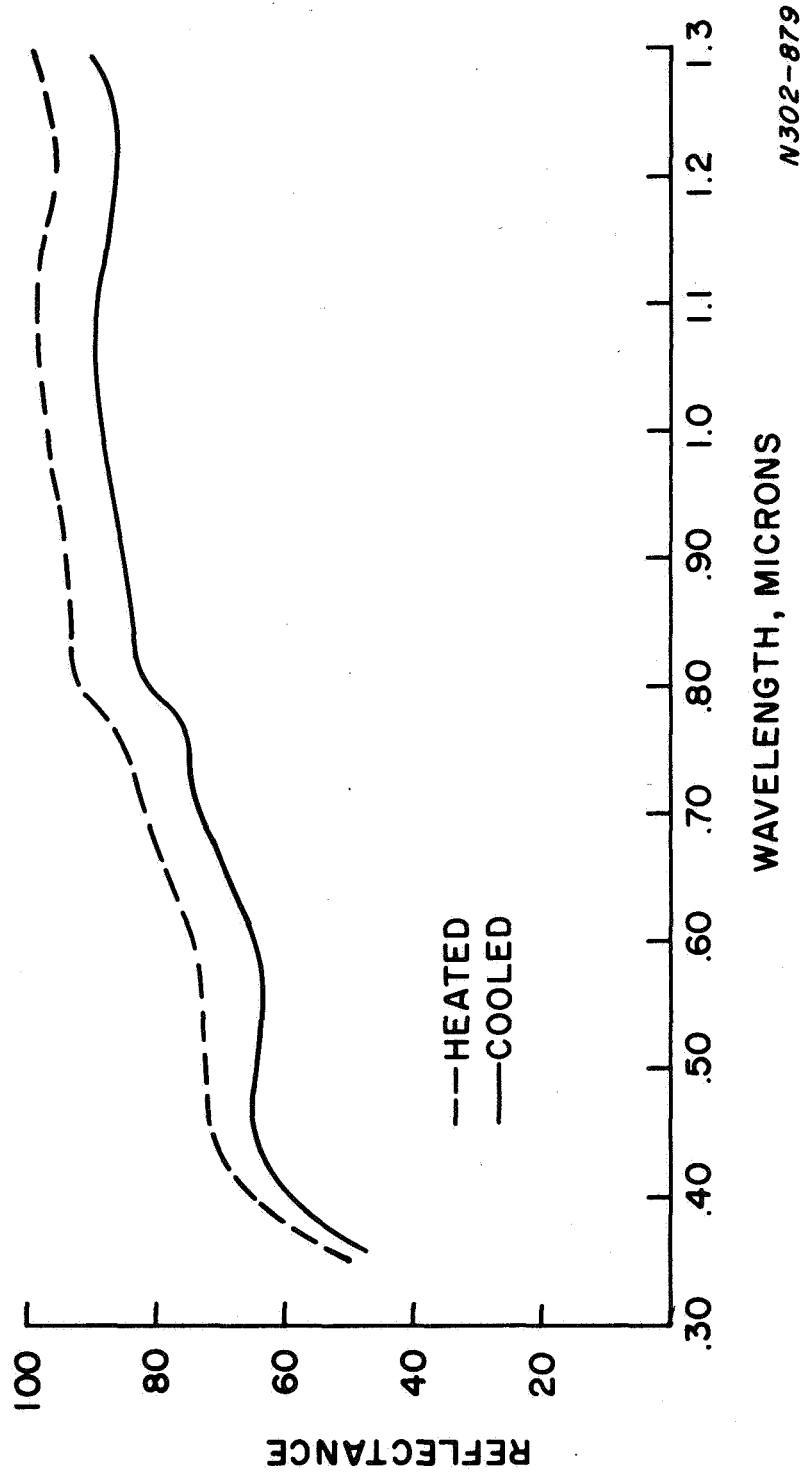
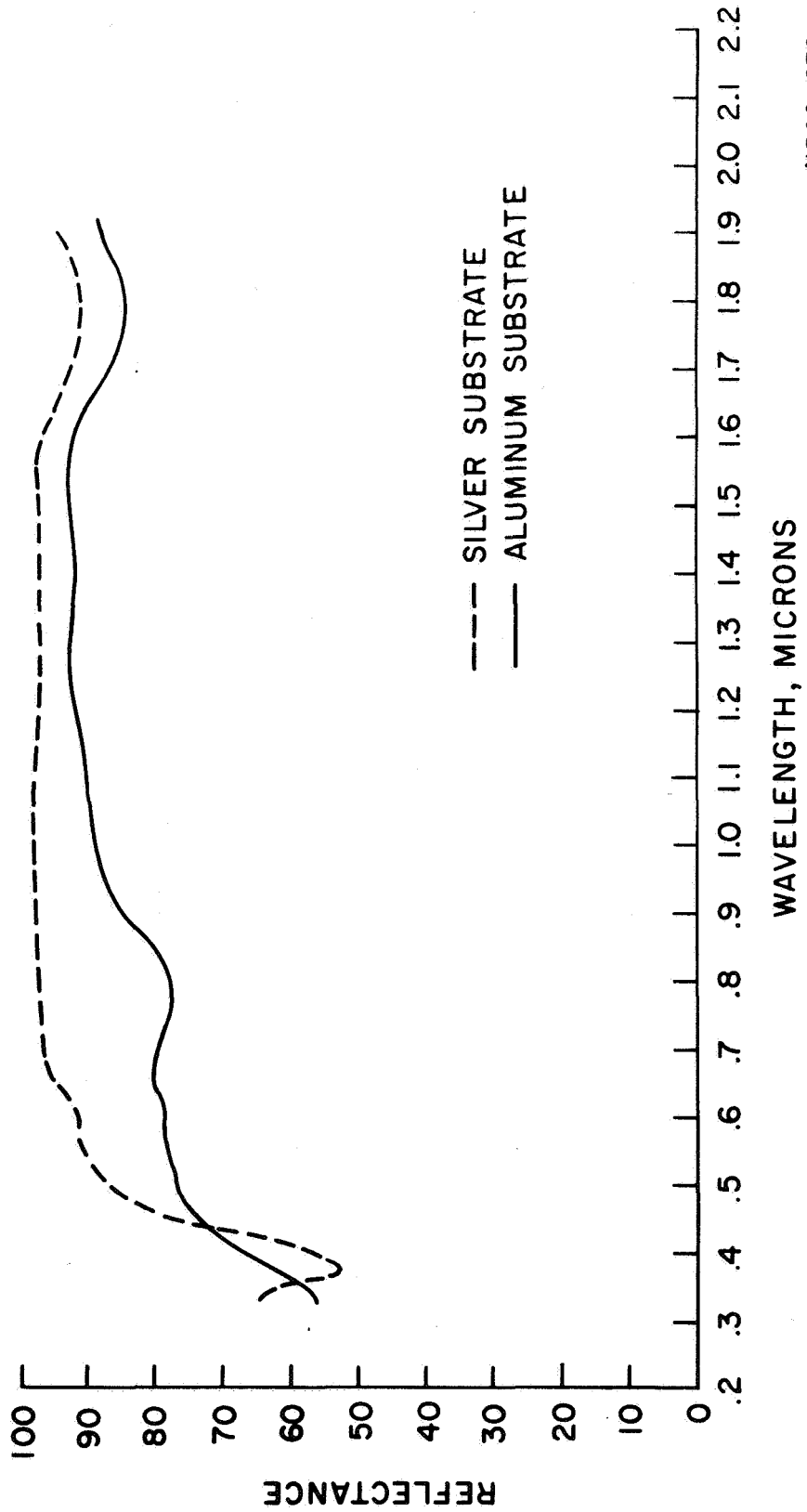


Figure 2. Reflection of an amyl stearate coating





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Figure 3. Reflection of amyl stearate coating on aluminum and on silver

preparation of the reflective substrate. Had the substrate under that sample been as reflective as the silver substrate under the sample shown in Figure 3, the observed temperature-dependent change in absorptance would have been about two-fold. But it was during irradiation studies that the greatest sample-to-sample variations occurred in amyl stearate coatings. The first such sample to be tested was irradiated for  $10^3$  ESH and  $10^8$  rads x-ray. Pressure in the system during irradiation remained in the  $10^{-8}$  to  $10^{-7}$  torr region, indicating little outgassing or degradation. But when the sample was removed from the vacuum chamber at the end of the irradiation, it was white and opaque up to at least  $50^\circ\text{C}$ . A second sample was irradiated in the same manner at pressures ranging from  $1 \times 10^{-7}$  torr to  $3 \times 10^{-8}$  torr. Adhesion to the substrate was lost at the points where the sample was clamped to the cooling block. Otherwise, the sample appeared relatively undamaged. The absorptance in the high temperature state had increased from 0.11 to 0.12. Faced with these contradictory results, we irradiated a third sample of the same formulation. After  $10^3$  ESH and  $10^8$  rads x-ray, the sample was partly yellow. The yellow part no longer adhered to the substrate, but the poly(vinyl butyral) and silicone layers of the coating were well bonded together. The discoloration appeared to be in the poly(vinyl butyral) and not in the silicone. It was not possible to say definitely whether the yellowing resulted from loss of adhesion and consequent overheating or whether the loss of adhesion was a consequence of degradation.

Finally, a fourth replicate sample was irradiated under the same conditions. In this sample, there was some loss of adhesion between the poly(vinyl butyral) and the substrate and between the poly(vinyl butyral) and the silicone. The latter was slightly brittle, somewhat opaque near the edges, but transparent in the center. There was slight discoloration of the silicone but none was apparent in the poly(vinyl butyral). The phase-change was spotty, irregular, and slow. No optical measurements were made.

#### D. COATINGS IRRADIATION SYSTEM

Candidate phase-change coatings were screened by an examination of their stabilities to ultraviolet and x-radiation in vacuum. Irradiations were conducted in the apparatus shown in Figure 4. The vacuum system has an adsorption fore-pump and a triode ion pump. It normally operates at about  $1 \times 10^{-8}$  torr without bakeout. The ultraviolet source was a high pressure xenon lamp powered by a constant current supply. The light was filtered through 5 cm of "ultra-pure" water to remove light above  $0.9\mu$ . It entered the vacuum chamber through a sapphire window. Intensity measurements were made with a calibrated copper-constantan thermopile. X-rays were supplied by an XRD-6 generator operated at 4.5 ma and 46 kv. Voltage ripple was less than 3%, and current was regulated to  $\pm 0.2$  ma. The x-ray intensity at the sample position was determined by dimethoxy diphenyl-bisazobis-8-amino-1-naphthol-5, -

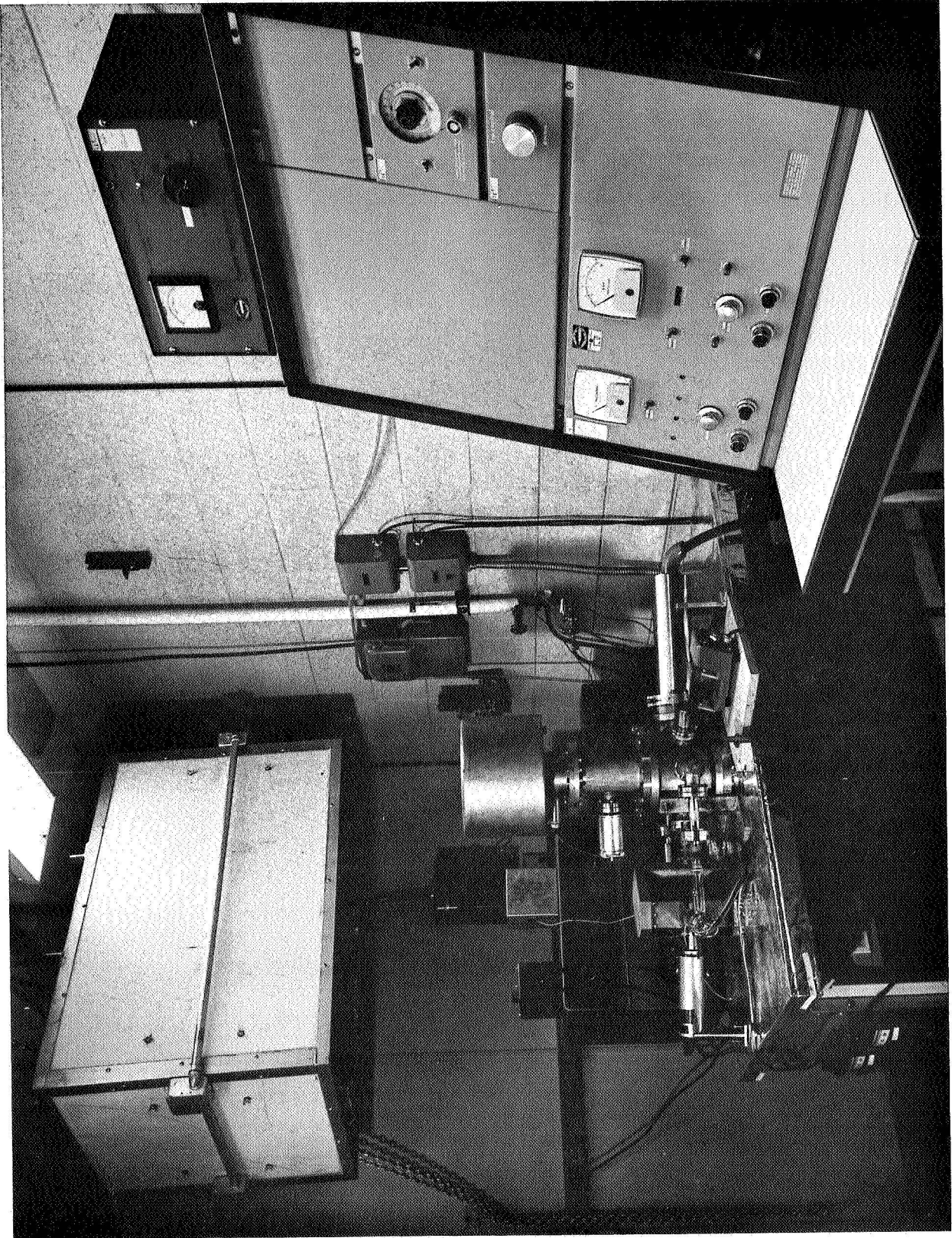


Figure 4. Sample Irradiation System

7-disulfonic acid dye dosimetry using the  $\text{Co}^{60}$  calibration curve of Henley and Richman<sup>(2)</sup>. This method was chosen because of the limited space available at the sample position. The samples consisted of 1-inch diameter chrome-plated steel discs coated with vapor-deposited aluminum or silver over which was applied a layer of the candidate coating. The normal procedure was to place one sample in the chamber and to evacuate the system overnight.

Irradiations were normally conducted at five suns intensity and 0.5 Mrad per hour for a period of two hundred hours. Absorptance measurements were made on the samples after removal from the vacuum chamber. While measurements made in this fashion cannot detect oxygen-sensitive radiation damage, the errors introduced are not likely to be as important in the cases studied in this work as they are in coatings pigmented with metal oxides or other semi-conductor pigments.

## E. MEASUREMENT OF OPTICAL PROPERTIES

### 1. Measurement Techniques

The measurement of optical properties below room temperature involves some experimental difficulties, the most significant of which is the condensation of water or ice on the sample surface. This results in large changes in reflectance which obscure the actual changes occurring in the coating due to crystallization. Though not always entirely satisfactory, the flowing of dry nitrogen over the sample face or making the measurement in a dry bag has minimized the error due to this source.

Difficulty was also encountered in attempting to cool the sample in the Gier Dunkle integrating sphere. The sample mount, being located in the center of the sphere on a rotating shaft, makes providing liquid cooling extremely cumbersome. Attempts to use a thermoelectric cooling element also failed since we were unable to dissipate the heat from the back face of the element, and the sample temperature remained well above the desired levels. The Gier Dunkle portable reflectometer, which can be used to measure room temperature reflectance, is not suitable for low temperature measurement since the detector is a thermopile and is therefore sensitive to sample temperature.

The apparatus that has been found suitable for making reflectance measurements at low temperature is a sphere in which the sample is located on the sphere wall and its temperature is therefore readily controlled. Access ports permit a continuous flow of dry nitrogen through the sphere which minimized the frost problem. The principal limitation of this technique is the intrinsic error associated with the measurement of slightly diffuse samples due to energy being reflected out the entrance ports. This error,

however, is not expected to be more than a few percent of the total reflectance and therefore not critical in this application.

The measurement of diffuse transmission as a function of temperature, however, was accomplished with a Gier Dunkle integrating sphere operated in the transmission mode as shown schematically in Figure 5. While this technique does not provide a measure of solar absorptance, it is useful for kinetics studies.

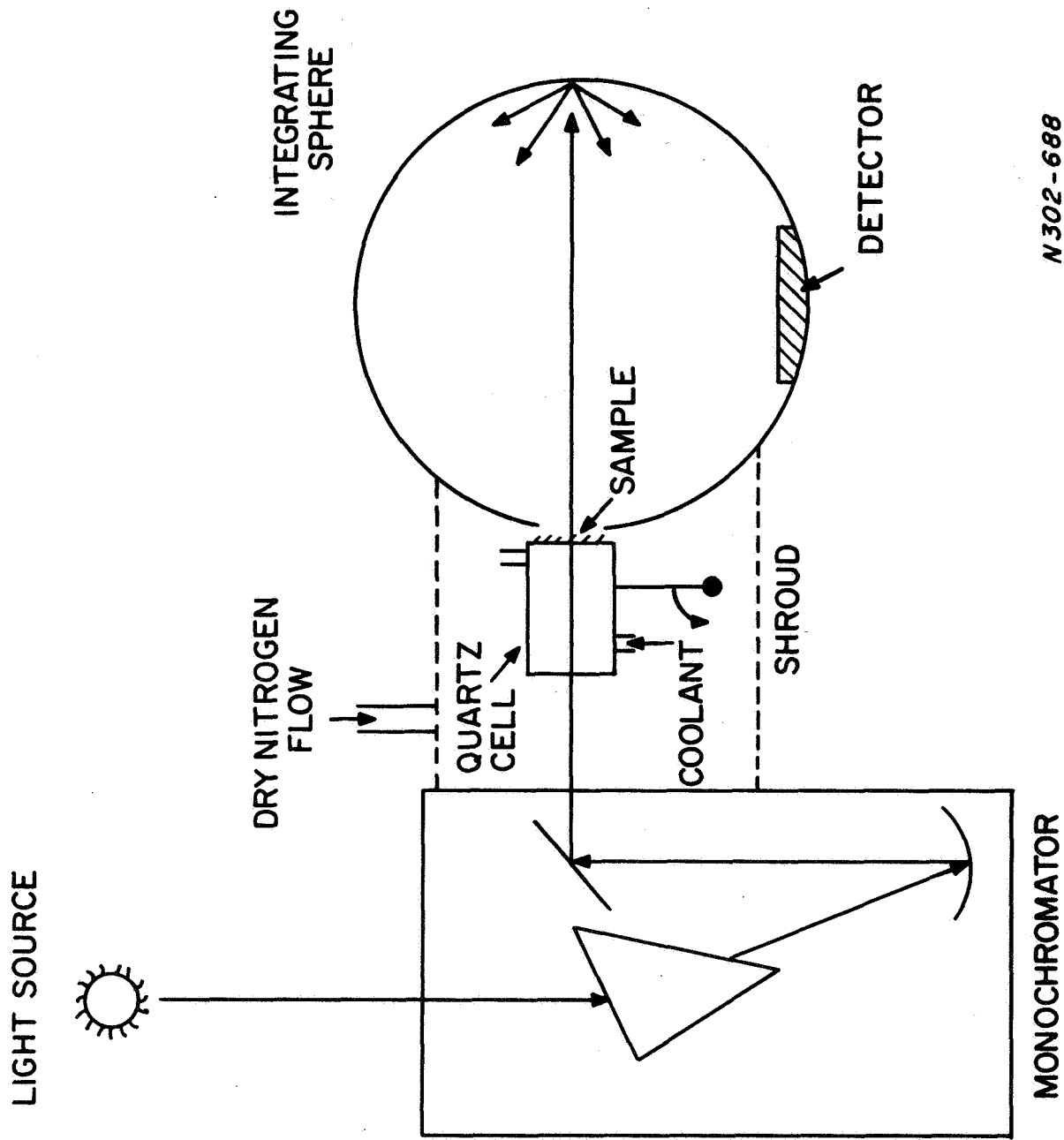
## 2. Results

The optical behavior of many phase-change coatings is described by the hysteresis loop reported previously for the dioctadecyl phosphite/poly-(vinyl butyral) system<sup>(1)</sup>. The optical properties at any temperature depend on length of time the sample has been at that temperature and on whether the sample is being cooled or heated. This is best illustrated by reference to Figure 6 which shows the transmission vs. temperature curve for a coating containing amyl stearate and stearic acid. As is indicated, the data points represent the transmission ten minutes after achieving temperature on the heating curve and two hours after on the cooling curve. While it is possible that if sufficient time is allowed these two curves will become congruent, the amount of time required is considerably longer than that prescribed in the work statement. A clear picture of the difference in crystallization rates at 10°C and 15°C is shown in Figure 7. It is this temperature-dependence of rate which results in the hysteresis loop previously described, since equilibrium transmission is attained relatively rapidly on heating.

An observation regarding crystallization rates made earlier<sup>(1)</sup> indicated that the rate was markedly affected by the purity of the pigment. Figure 8 demonstrates the effect of purification on crystallization rate at 10°C for the amyl stearate system. The recovery (crystallization) rate was markedly decreased by zone refining. Infrared analysis indicated that the major impurity removed was stearic acid. The addition of about five percent of stearic acid to the zone-refined amyl stearate increased the rate of crystallization to a greater value than was observed with the original sample. We interpret these facts as an indication that stearic acid provides an efficient nucleation site for crystallization of the amyl stearate.

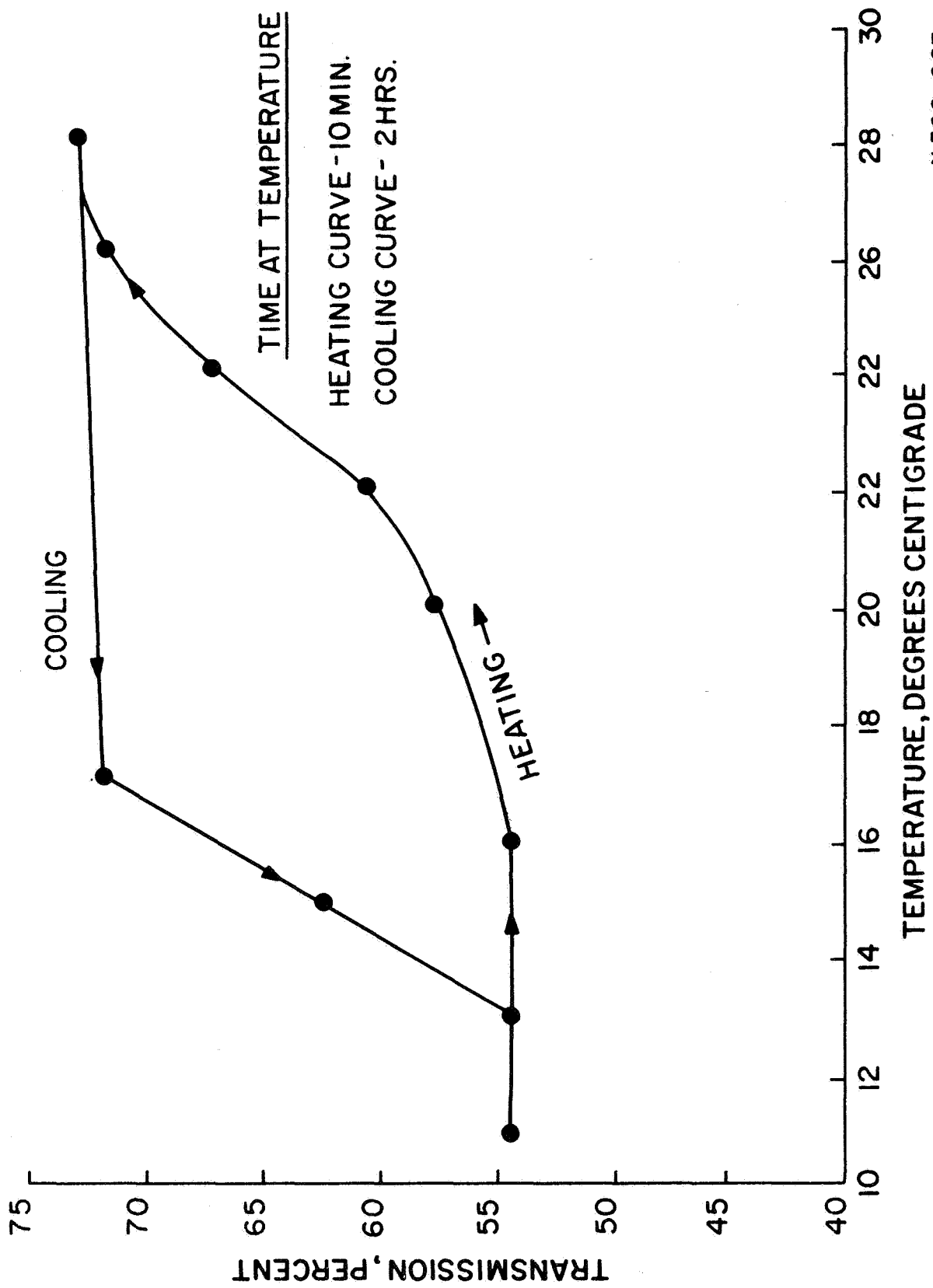
## 3. Substrate Effects

An effective means of altering the radiative properties of "phase-change" coatings is to utilize different metals as the substrate reflectors. Judicious choice of metal not only permits selecting the levels of solar absorptance between which the coating will cycle but may also improve the apparent radiation resistance of the coating.



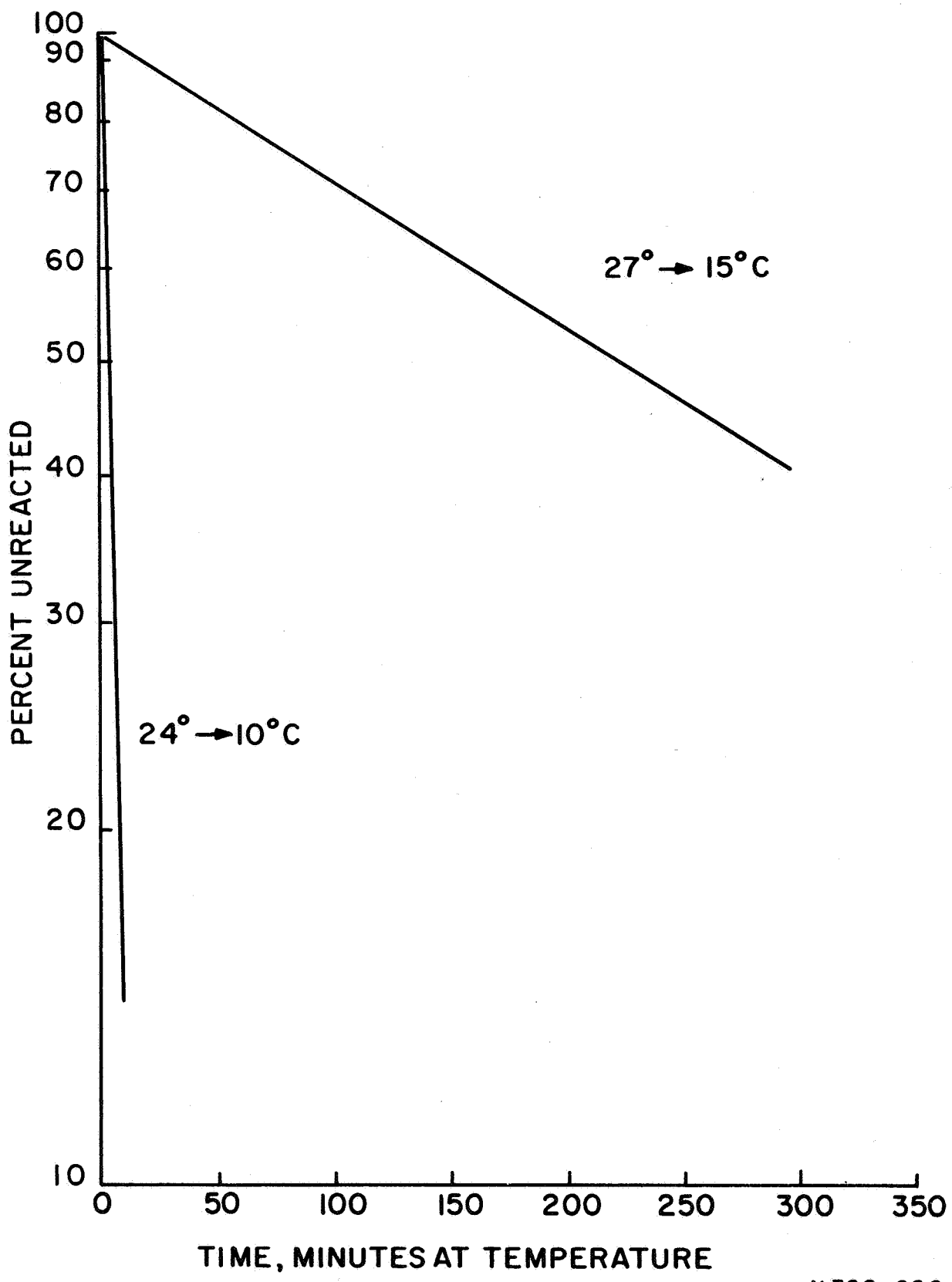
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Figure 5. Diffuse Transmission Apparatus



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Figure 6. Dependence on Temperature of the Transmission of an Amyl Stearate Coating



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Figure 7. Rate of Change of Transmission of an Amyl Stearate Coating at Two Temperatures



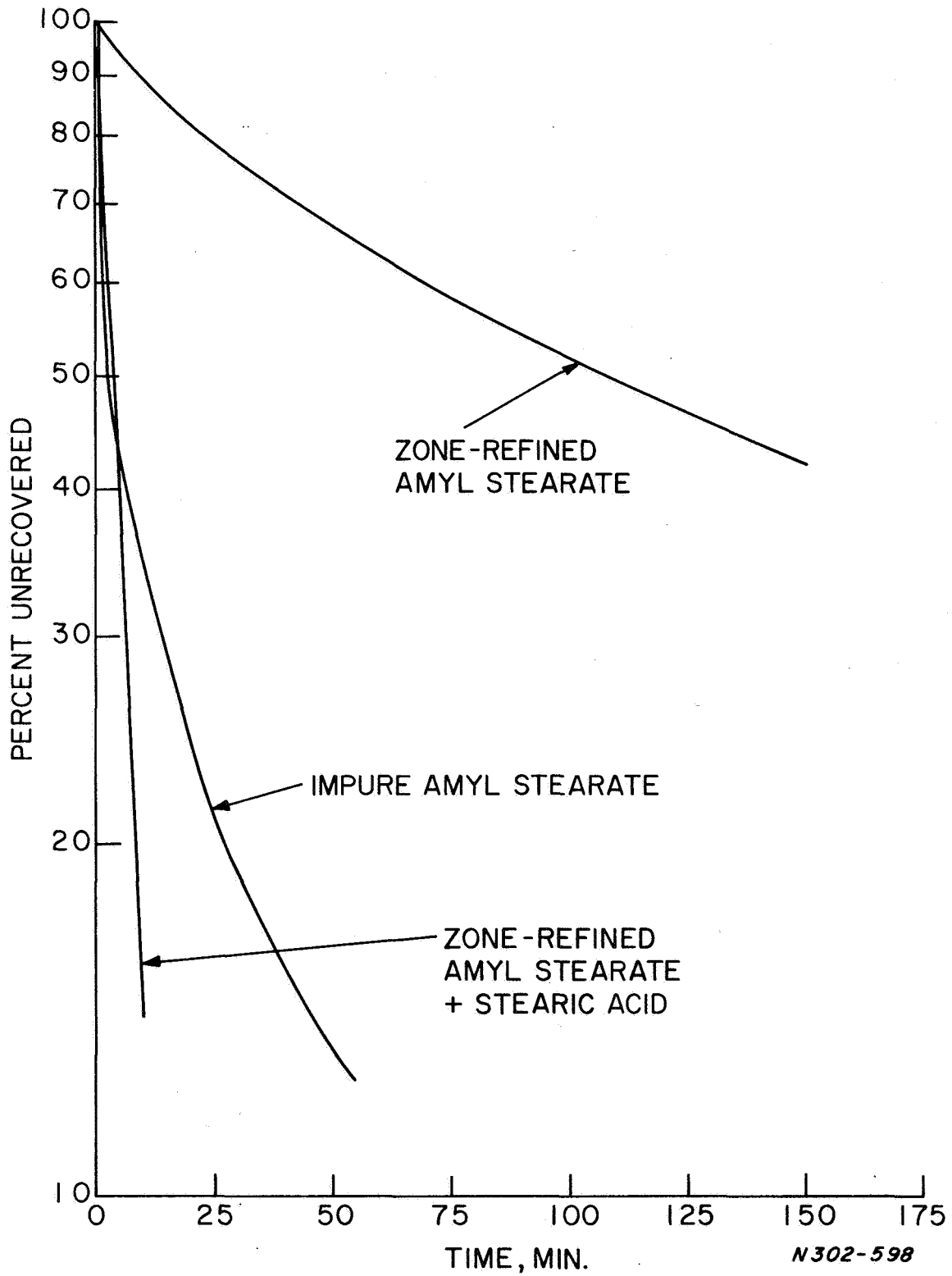


Figure 8. Recovery Kinetics of Amyl Stearate in Butvar at 10°C

The first statement is clearly shown in Figure 3 which shows the spectral reflectance at room temperature of an amyl stearate coating backed with aluminum and one backed with silver. The room temperature solar absorptances were 0.12 with silver backing and 0.21 with aluminum backing.

Improvements in apparent radiation resistance obtained by use of spectrally selective radiators have not as yet been experimentally demonstrated. The basic assumptions involved are that damage due to the radiation environment is confined to the coating itself and does not affect the metal reflector, and that the damage that occurs to the coating results in a change in absorption over a relatively narrow wavelength band (this appears true for the binders evaluated previously<sup>(1)</sup>).

A metallic reflector that absorbs in the spectral region where the change in coating absorption occurs will provide a coating whose solar absorptance will remain constant even though the absorption of the coating increases. Candidate reflectors for this type of coating system would be silver for damage below 0.4 microns, gold below 0.5 microns, and zinc for damage in the near infrared (about 1.0 micron), as well as others which have not as yet been evaluated.

#### IV. CONCLUSIONS

About a hundred formulations were made in the search for a room temperature phase-change coating. At least two formulations were identified which may prove satisfactory for missions of short duration, but further improvement will be necessary if they are to withstand the required thousand hours in space. Coatings of dilauryl phosphite in poly(vinyl butyral) undergo a phase-change between about 6°C and 20°C, but no overcoat has been found which is impermeable to the dilauryl phosphite. Coatings of amyl stearate in poly (vinyl butyral) performed well except for variable results in irradiation tests. The cause of this variability may be subject to correction.

Further work on the development of phase-change coatings should emphasize long lifetimes and in-situ measurements during irradiation testing. Requirements for rapid and repeated cycling should be of minor importance, with major emphasis on the development of the simplest and stablest system possible.

## V. REFERENCES

1. R. Griffin and B. Linder, "Development of Phase-Change Coatings for use as Variable Thermal Control Surfaces," NASA CR-66394, 1967.
2. E.J. Henley and D. Richman, Analytical Chemistry, 28, 1580 (1956).

# APPENDIX I

## Summary of Formulations

### I. Formulations with Butvar B98

<u>Pigment</u>	<u>Concentration,</u> <u>phr</u>	<u>Other Additives,</u> <u>phr</u>	<u>Comments</u>
Dilauryl phosphite, fraction 33A	25	Resoflex, 20	Transparent to -10°C
	50	Resoflex, 20	White at -10°C
	50		White at -10°C
	100		Phase-change between 6° and 20°C
	100	Cab-O-Sil, 0.5; silicone 391-15-170 overcoat	Same; failed after 250 cycles
	50	Hexamethoxymethyl- melamine, 10	Phase-change between 6° and 20°C
	100	Zeolite, trace; silicone 391-15-170 overcoat	Pigment on surface after both room temperature and oven cures
	100	Zeolite, trace; overcoat of PVB + hexamethoxy- methylmelamine	Pigment on surface
	100	RTV 602 overcoat	Pigment on top of silicone
	100	Overcoat of PVB + tolylene di-iso-cyanate	Most of opacity lost during 10 <sup>3</sup> cycles; pigment largely on surface
	100	Overcoat of PVB + hexa- methoxymethylmelamine	Most of opacity lost during 10 <sup>3</sup> cycles; pigment largely on surface
-----			
Dilauryl phosphite, fraction 33D	50		Transparent to 6° C
	100		Phase-change between 6° and 20°C
	100	Silicone 391-15-170 overcoat	Baked 1 hr. at 75°C
	100	Cab-O-Sil, 0.5; silicone 391-15-170 overcoat	Failed after 250 thermal cycles in vacuum
	100	RTV-602 overcoat	Many bubbles in coating
	100	Formvar overcoat	Hazy; overcoat shrinks
-----			

APPENDIX I (Cont.)

<u>Pigment</u>	<u>Concentration,</u> <u>phr</u>	<u>Other Additives,</u> <u>phr</u>	<u>Comments</u>
Dilauryl phosphite, Aldrich Chemical	50	Zeolite, 0.1; silicone 391-15-170 overcoat	Silicone would not cure
	100	Zeolite, 0.1; silicone 391-15-170 overcoat	Silicone cured at room temperature
	100	Zeolite, 0.1; PVB + hexamethoxymethyl- melamine overcoat	Similar to sample made with fraction 33A
	50	Zeolite, 0.1; hexa- methoxymethylmelamine, 10; silicone 391-15-170 overcoat	Very slow phase-change at $-10^{\circ}\text{C}$
-----			
Trilauryl trithiophosphite	25	Resoflex, 20	Cloudy to $67^{\circ}\text{C}$
	50	Resoflex, 20	Cloudy to $67^{\circ}\text{C}$
	100	Resoflex, 20	Globules of pigment
	12.5	Resoflex, 10	Phase-change between $0^{\circ}$ and $25^{\circ}\text{C}$
	15		Same; OK after $10^3$ cycles
	15	Resoflex, 20	Phase-change but cloudy at RT
	12.5	Resoflex, 20; PVB + hexamethoxymethyl- melamine overcoat	$\alpha = .29 \neq .17$ After $10^3$ cycles $\alpha = .29 \neq .19$
	12.5	PVB + hexamethoxy- methylmelamine overcoat	$\alpha = .31 \neq .16$ After $10^3$ cycles $\alpha = .31 \neq .17$
	12.5	Novacite, ~1	Slow phase-change; uneven change to
	10		Slow phase-change      opaque state

APPENDIX I (Cont.)

<u>Pigment</u>	<u>Concentration,</u> <u>phr</u>	<u>Other Additives,</u> <u>phr</u>	<u>Comments</u>
Trilauryl trithiophosphate (continued)	12.5	PVB + hexamethoxy- methylmelamine over- coat	TL TTP zone-refined; m.p. 27°C, n <sub>D</sub> <sup>25</sup> 1.5014. Silicone overcoat would not cure. Some samples have good phase-change. Others remain transparent.
	12.5	PVB + hexamethoxy- methylmelamine	Cycled 10 <sup>3</sup> times without apparent damage
	12.5		Ethanol/toluene solvent; could not spray. Some brushed coatings satisfactory.
	12.5		Isobutanol/xylene solvent; all samples poor.
	12.5		Isopropanol/xylene solvent; sprays and brushes well.
	12.5	Zeolite, 0.5	Isopropanol/xylene solvent; sprays and brushes well.
	12.5	Zeolite, 0.1; PVB + hexamethoxymethyl- melamine overcoat	Cycled 10 <sup>3</sup> times without apparent damage. After 10 <sup>3</sup> ESH and 10 <sup>8</sup> rads, α <sub>g</sub> increased from .13 to .20.
	12.5	Zeolite, 0.1; hexamethyl phosphoric triamide, 2; PVB + hexamethoxy- methylmelamine overcoat	First sample turned brown on irradi- ation. Second sample could not be irradiated because of excessive out- gassing. Third sample irradiated to < 220 ESH. Turned brown and distorted.

APPENDIX I (Cont.)

<u>Pigment</u>	<u>Concentration,</u> <u>phr</u>	<u>Other Additives,</u> <u>phr</u>	<u>Comments</u>
Propyl sulfone	25		Transparent
	50		Transparent
	100		Opaque at 6°C; phase-change around 25°C
	100	PVB + hexamethoxy-methylmelamine overcoat	Transparent to -10°C
	100	Zeolite, 0.1	Phase-change around 25°C. No improvement noted due to zeolite.
	100	Resoflex, 10; zeolite, 0.1; PVB + hexamethoxy-methylmelamine overcoat	Transparent to -10°C.
-----			
Tridodecylamine	50	Resoflex, 20	Not homogeneous
	25	Resoflex, 10	Layer of liquid on top
	15	Resoflex, 20	Not transparent
	12	Resoflex, 5	Phase-change in refrigerator; transparent at room temperature
	12	Resoflex, 5; silicone 391-15-170 overcoat	Less transparent than above. Good phase-change. Same after 10 <sup>3</sup> thermal cycles.
	12	Resoflex, 5; PVB + hexamethoxymethylmelamine overcoat	Same as above.
-----			
Tridodecylamine, zone-refined	12	Resoflex, 5	Good phase-change
-----			
All formulations with tridodecylamine turn brown on heating to 100°C or on standing for several weeks.			



APPENDIX I (Cont.)

<u>Pigment</u>	<u>Concentration,</u> <u>phr</u>	<u>Other Additives,</u> <u>phr</u>	<u>Comments</u>
2-Tridecanone	25	Resoflex, 20	Little change in freezer
	50	Resoflex, 20	Good change in refrigerator; failed in vacuum
	50		Little change
-----			
Amyl stearate	25		Good phase-change, not completely transparent
	25	Resoflex	Slightly better than above
	20	Resoflex, 20	$\alpha = .28 \pm .19$
	16.7	Resoflex, 20	$\alpha = .22 \pm .18$
-----			
Zone-refined amyl stearate	20	Resoflex, 20	Very poor recovery
-----			
Octadecyl acetate	50	Resoflex, 10; zeolite, 0.1	Pigment separates from binder on cycling
	30	Resoflex, 10; zeolite, 0.1	No phase-change after removal of surface pigment
-----			
Didecyl sebacate	25	Resoflex, 20; zeolite, 0.1	Phase-change near room temp- erature, but does not get very opaque
	50	Resoflex, 20; zeolite, 0.1	Pigment separates
-----			

APPENDIX I (Cont.)

II. Formulations with Butvar B76

<u>Pigment</u>	<u>Concentration,</u> <u>phr</u>	<u>Other Additives,</u> <u>phr</u>	<u>Comments</u>
Amyl stearate	17	Resoflex, 20	Not completely transparent
Zone-refined amyl stearate	17	Resoflex, 20	Very slow recovery; not completely transparent
Zone-refined amyl stearate	17	Resoflex, 20	$\alpha = .07 \rightleftharpoons .12$
+ 5% stearic acid	17	Resoflex, 20; Cab-O-Sil 0.5	Same as above
	17	Resoflex, 50	Opaque
	17	Resoflex, 10	Excellent phase-change at 6°C
	25	Resoflex, 10	Excellent phase-change; discolored silver discs
	25	Resoflex, 10	Ethanol/toluene solvent; could not make good samples
	25	Resoflex, 10; silicone 391-17-150 overcoat	Isopropanol/xylene solvent; silicone turned white during irradiation; absorbance of second sample increased from 0.11 to 0.12 during irradiation
	25	Resoflex, 10	Discolored silver discs
	25	Resoflex, 10; PVB + hexamethoxymethyl-melamine overcoat	Cycled 10 <sup>3</sup> times without apparent damage
Octadecyl acetate	30	Resoflex, 5; zeolite, 0.1	Pigment on surface

APPENDIX I (Cont.)

<u>Pigment</u>	<u>Concentration,</u> <u>phr</u>	<u>Other Additives,</u> <u>phr</u>	<u>Comments</u>
Didecyl sebacate	25	Resoflex, 10	Pigment mostly on surface
	50	Resoflex, 10	Pigment mostly on surface
-----			
Resoflex R296	50		Opaque to 50°C
	40		Opaque to 50°C
	30		Opaque to 50°C
	20		Cloudy at room temperature
	10		Cloudy at -10°C; transparent at room temperature
-----			
Dilauryl phosphite	100	Resoflex, 10; zeolite, 0.1	Pigment largely on surface
-----			

APPENDIX I (Cont.)

III. Miscellaneous Formulations

<u>Binder</u>	<u>Pigment</u>	<u>Concentration, phr</u>	<u>Other Additives, phr</u>	<u>Comments</u>
RTV 602	Dilauryl phosphite	25		Opaque, inhomogeneous, shrank
	Propyl sulfone	10		Would not cure
		5		Opaque; cured with difficulty
-----				
Formvar	Dilauryl phosphite	25		Cloudy; no phase-change; poor adhesion
		25	Resoflex, 20	Same as above
-----				
Formvar/Butvar 5:1	Dilauryl phosphite	25		Cloudy to 70°C
-----				
Formvar/Butvar 1:1				All inhomogeneous;
1:1			Resoflex	globules (of Formvar?) visible through microscope
1:2				
1:5				
1:10				
10:1				Homogeneous, clear; poor adhesion to aluminum
5:1				
-----				
Formvar			Resoflex, 20	Clear, homogeneous
-----				
Formvar	Trilauryl trithiophosphite	10		Yellow, not very transparent; no adhesion to aluminum
-----				
Silicone 391-17-150	Propyl sulfone	~10		Most of pigment on surface

## APPENDIX II

### LIST OF MANUFACTURERS OR SUPPLIERS OF IMPORTANT MATERIALS

Silicone 391-15-170 - General Electric Company, Silicone Products Department

"Formvar" poly(vinyl formal) - Monsanto Company

"Butvar" poly(vinyl butyral) - Monsanto Company

Trilauryl trithiophosphite - Hooker Chemical Corporation

Dilauryl phosphite - Hooker Chemical Corporation

"Cab-O-Sil" - Cabot Corporation

"Resoflex" - Cambridge Industries Company

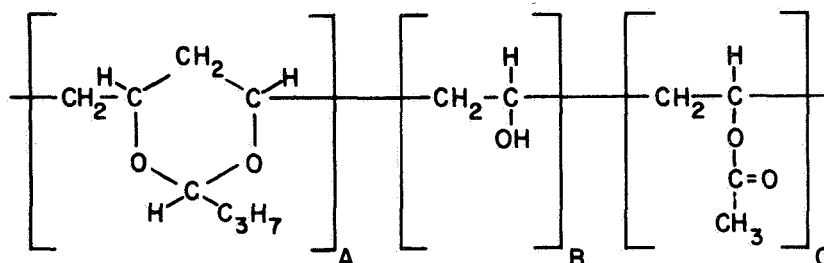
Hexamethoxymethylmelamine - American Cyanamid Company

Zeolite - Linde Company

"Novacite" - Malvern Minerals Company

APPENDIX III  
 CHEMICAL STRUCTURES AND PHYSICAL PROPERTIES  
 OF IMPORTANT MATERIALS

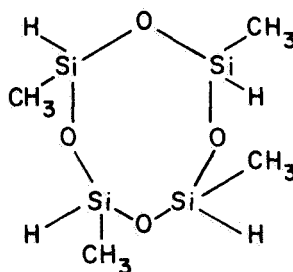
1. Poly(vinyl butyral)



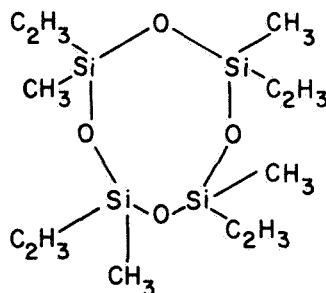
The proportions of A, B, and C are controlled and they are randomly distributed along the molecule. In Butvar B98, the proportions are 80%, 18-20%, and 0-2% respectively. In Butvar B76 they are 88%, 9-13%, and 0-2.5% respectively.

2. Silicone 391-15-170

A condensation polymer of methyl hydrogen tetramer



and methyl vinyl tetramer

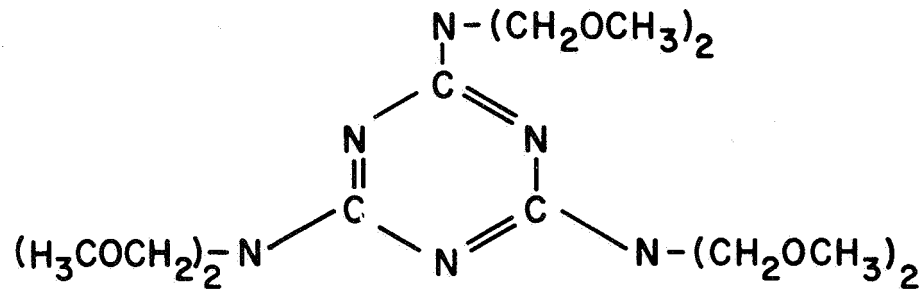


Cured films are hard, mar resistant, and non-yellowing even after exposure to intense ultraviolet radiation. They are recommended for use as protective coatings, as solvent barriers, and as means of improving the surface finish of other components.

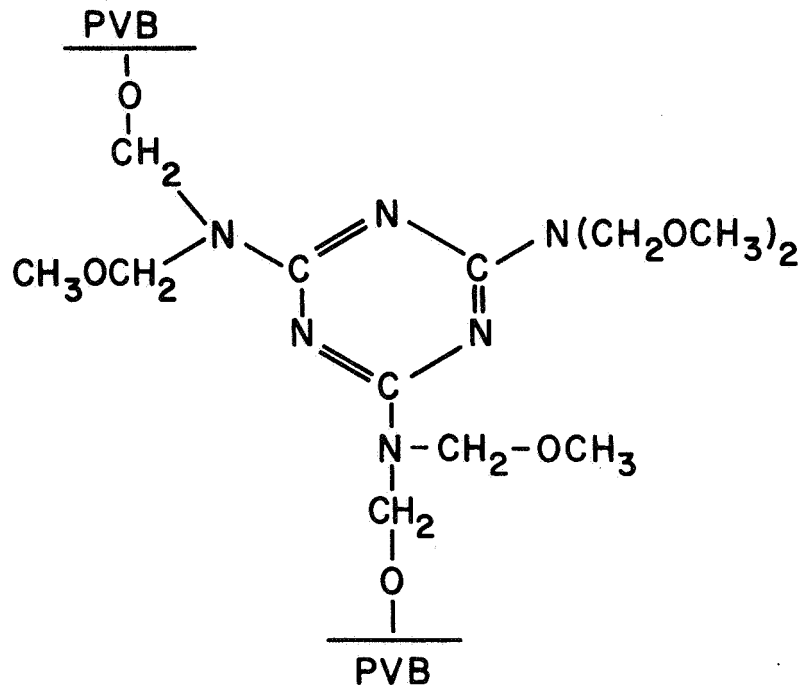
3. Resoflex R-296

This plasticizer is a resinous, saturated alkyd whose exact chemical structure is not known. It is a pale liquid with a Gardner-Holt viscosity Z-2 and a refractive index of 1.471.

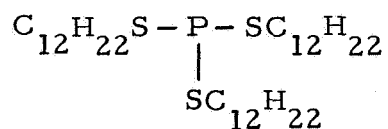
4. Hexamethoxymethylmelamine



Poly(vinyl butyral) can be cross-linked by reaction of hydroxyl groups with the melamine to give a structure which can be represented as:

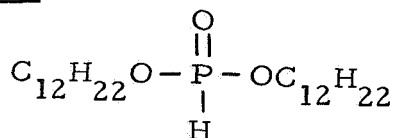


5. Trilauryl trithiophosphite



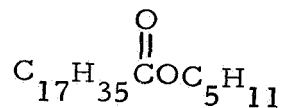
This material, used as a pigment, has a molecular weight of 634, melts at 26.8-27.0°C and has a refractive index  $n_D^{25} = 1.5008$ .

6. Dilauryl phosphite



This pigment has a molecular weight of 412, melts at 25°C, and has a refractive index  $n_D^{25} = 1.4487$ .

7. Amyl stearate



This material has a molecular weight of 354.6 and melts at 29-30°C.