Gulf Coast of southern Veracruz and Tabasco in Mexico, and we suggest that the real transition to village life took place there and not in the dry Mexican highlands, where maize was domesticated initially (17).

Conclusion

The interpretation of archeological remains through a fine-scale analysis of small ecological zones throws new light on the move toward sedentary life in Mesoamerican prehistory. In our terms, the basic difference between peoples who subsist on wild foods and those who dwell in permanent villages is that the former must exploit a wide variety of small ecological niches in a seasonal pattern-niches which are usually scattered over a wide range of territory-while the latter may, because of an effective food production, concentrate on one or on only a few microenvironments which lie relatively close at hand.

Fine-scale ecological analysis indicates that there never was any such thing as an "agricultural revolution" in Mesoamerica, suddenly and almost miraculously resulting in village life. The gradual addition of domesticates such as maize, beans, and squash to the diet of wild plant and animal foods hardly changed the way of life of the Tehuacán people for many thousands of years, owing to a general paucity of the environment, and seasonal nomadism persisted until the introduction of irrigation. It probably was not until maize was taken to the alluvial, lowland littoral of Mesoamerica, perhaps around 1500 B.C., that permanently occupied villages became possible, through reduction of the number of microenvironments to which men had to adapt themselves.

References and Notes

- 1. Mesoamerica is the name given to that part Mexico and Central America which was
- of Mexico and Central America which was civilized in pre-Columbian times. For an excellent summary of its prehistory, see G. R. Willey, Science 131, 73 (1960).
 2. R. S. MacNeish, Science 143, 531 (1964).
 3. See C. A. Reed and R. J. Braidwood, "Toward the reconstruction of the environmental sequence of Northeastern Iraq," in R. J. Braidwood and B. Howe, "Prehistoric Investigations in Iraqi Kurdistan." Oriental sequence of Northeastern Iraq," in R. J. Braidwood and B. Howe, "Prehistoric In-vestigations in Iraqi Kurdistan," Oriental Institute, University of Chicago, Studies in Ancient Oriental Civilization No. 31 (1960), 163. Reed and Braidwood also convincing-
- b) reject the technological deterministic approach of V. G. Childe and his followers. See B. J. Meggers, Am. Anthropologist 56, 801 (1954), for an environmental-deterministic view of the constraining effects of tropical forests on human cultures. 5. See F. Barth, *ibid.* 58, 1079 (1956), for a
- microenvironmental approach by an ethnolo-gist to the exceedingly complex interrelationships between sedentary agriculturists, agri-culturists practicing transhumant herding, and nomadic herders in the state Swat, of Pakistan.
- Steward, "Basin-Plateau Aboriginal 6. J. H. Sociopolitical Sociopolitical Groups," Smithsonian Bur. Am. Ethnol. Bull. 120 (1938).
- Bur. Am. Ethnol. Bull. Similary This. Bur. Am. Ethnol. Bull. 120 (1938).
 The pitfalls of searching for ethnological data relevant to archeological problems among cultures far-flung in time and space are stressed by J. G. D. Clark, Prehistoric Europe, The Economic Basis (Philosophical Library, New York, 1952), p. 3.
 See W. W. Taylor, Ed., "The identification of non-artifactual archaeological materials," Natl. Acad. Sci.-Natl. Res. Council Publ. 565 (1957). For a general article on the analysis of food remains in archeological deposits see R. F. Heizer in "Application of quantitative methods in archaeology," Viking Fund Publications in Anthropology No. 28 (1960), pp. 93-157.
 P. C. Mangelsdorf, R. S. MacNeish, W. C.

Gallinat. Science 143, 538 (1964). We thank Gallinat, Science 143, 538 (1964). We thank Dr. MacNeish for permission to use un-published data of the Tehuacán Archaeologi-cal-Botanical Project in this article.
10. R. S. MacNeish, Second Annual Report of the Tehuacán Archaeological-Botanical Proj-ect (Robert S. Peabody Foundation for Archaeology, Andover, Mass., 1962).
11. The research discussed in this and the following paragraph was carried out by Flannery as staff zoologist for the Tehuacán project during the field seasons of 1962 and

- project during the field seasons of 1962 and 1963; see K. V. Flannery, "Vertebrate Fauna and Prehistoric Hunting Patterns in the Tehuacán Valley" (Robert S. Peabody Foundation for Archaeology, Andover, Mass., in press); —, thesis, Univ. of Chicago, in preparation.
- M. D. Coe, "La Victoria, an early site on the Pacific Coast of Guatemala," *Peabody Museum, Harvard, Papers No.* 53 (1961). 13. The study was carried out largely bv Flannery.
- 14. The final report on Salinas La Blanca by Coe and Flannery is in preparation. The reand Flannery is in preparation. The re-search was supported by the National Sci-ence Foundation under a grant to the ence Foundation under a grant to the Institute of Andean Research, as part of the program "Interrelationships of New World Cultures." The oldest culture in the area is the Ocós phase, which has complex ceramics and figurines; the paleoecology of Ocós is less well known than that of directly follows it in time. Cuadros, which
- P. C. Mangelsdorf, who has very kindly examined these maize specimens, informs us that they are uncontaminated with *Tripsacum*, and that probably all belong to the primitive lowland race, Nal-Tel.
- To paraphrase the concept of "primary forest efficiency," developed by J. R. Cald-well ["Trend and Tradition in the Eastern United States," Am. Anthropol. Assoc. Mem. 16. United States," Am. Anthropol. Assoc. Men. No. 88 (1958)], we might think of the Cuadros phase as leaning to a "primary lagoon-estuary efficiency." We might think the same of the Ocós phase of the same region, which may date back to 1500 B.C.
- which may date back to 1500 B.C. 17. An additional factor which may in part account for the priority of coastal Guatemala over Tehuacán in the achievement of a sedentary mode of life is the presence of an extensive system of waterways in the former region, which might have made it less neces-sary for local communities to move to productive sources of food. By means of conset a few persons could have brought cances, a few persons could have brought the products of other niches to the village. However, our evidence indicates that the Cuadros people largely ignored the possibilities of exploiting distant niches.

Thermal Control in Space Vehicles

Organic coatings provide convenient and relatively inexpensive means of regulating interior temperature.

A. L. Alexander

Since the initial space probes and satellites were designed, the control of temperatures likely to accrue within the vehicles themselves has received increasing attention. As designs become

more sophisticated, requirements for reliable thermal control have increased. In an early review of methods for controlling temperatures in satellites and space vehicles, Camack and Edwards (1) outlined quite precisely the necessity for temperature control. Temperatures of satellites and spacecraft must be controlled reliably to satisfy requirements of internal instruments and payloads-especially man. For example, electrical components have highly restrictive temperature limitations and, to a considerable degree, dictate the thermal design of the vehicle. Transistor networks are useful only btweeen 0° and about 60°C. Some batteries will operate efficiently only within quite narrow temperature limits, and nearly all biological processes must be maintained within a range of about 40°C. The conversion efficiency of silicon solar cells, used at present for photovoltaic conversion of solar to electrical energy, increases markedly as temperature is decreased. Many mechanical functions may be affected or impaired by extremely high or low temperature, and structural alignments in optical systems can similarly be disturbed. Finally, living organisms require extremely precise and reliable temperature regulation. For example, 109°F is the highest temperature allowed in manned spacecraft (2).

Thermal energy affecting the temperature of a vehicle in space derives from two sources-(i) internal generation, and (ii) absorption of incident radiation or emission (or both) from the sun and other celestial bodies. (Radiation from the background of space itself is negligible, since its effective temperature is so low as to be insignificant.) Therefore, temperatures encountered by spacecraft are determined by an energy exchange between these two sources. By establishing and solving appropriate energy-balance equations, these values may be calculated.

Methods of Thermal Control

The two fundamental methods for controlling temperatures of spacecraft may be classified as passive and active. Passive thermal control, for a variety of reasons, has many advantages and is attained through appropriate geometrical design of the vehicle and a judicious selection of materials possessing the requisite physical and thermal properties. Passive control requires neither power nor working parts. It is achieved through the use of materials selected for their thermal properties (radiation, conduction, and emission) and their geometrical design, and sometimes through the use of materials whose thermal behavior during a phase change makes them useful as heat sinks. It is my purpose in this discussion to examine a class of materials designed for application to the surfaces of spacecraft-materials whose thermal and optical properties may be readily regulated and adjusted to provide conditions of thermal stability within the vehicle.

Certain advantages of passive over active thermal control become obvious when one considers that the latter requires the dynamic employment of temperature-induced physical changes

including, in materials. generally, changes either in power or in moving parts. The application of an active system involves the use of thermostats and heaters, the use of fluid refrigeration systems, and perhaps the inclusion of bimetallic strips to control shutter systems. Each of these subsystems lessens reliability by introducing the possibility of malfunction of bearing surfaces in moving parts or by adding critical weight to the design. On the other hand, an active thermal control system can be made to correct for alterations in the thermal behavior of a space vehicle influenced by extraterrestrial environments. Since much more precise control is available through active-control techniques, life-support systems require active thermal control. As a practical measure, however, the two systems can be combined for enhanced efficiency, to utilize the inherent advantages of each.

Regardless of whether active or passive control is used, control requirements are influenced by outer-surface temperature. Surface temperatures are, in turn, determined by the thermalradiation characteristics of the surface, the external environment, vehicle and orbit geometrics (time in the earth's shadow), and internal power generation. The fact that surface temperatures can be made to fall anywhere within quite a wide range by proper surface preparation and selection of finishes has been discussed quite extensively (3). For this purpose, carefully designed coatings are applied to the surfaces of the vehicle. These coatings may be either organic or inorganic, but they must be so put together that there is a balance of properties. Too often it has not been clearly stated that radiation characteristics (often referred to simply as the solar absorptivity α_s , the low-temperature or infrared emissivity ϵ , and the ratio α_s/ϵ) affect the heat balance of the vehicle in a complex fashion. The difficulties in developing and maintaining stable coatings have not always been emphasized sufficiently. Research now being done at the Naval Research Laboratory has been intimately concerned with this latter problem.

Thus, by maintaining a proper balance between absorbed solar radiation and the heat energy emitted radiantly from the vehicle to cold space, almost any required temperature within the vehicle may be readily maintained. This balance, then, is a function of the optical properties and the temperature of the exterior surfaces of the craft. Further, there are two spectral regions of major interest, one between approximately 0.2 micron and 3.0 microns, wherein over 98 percent of the sun's energy is emitted, and the other beyond 3.0 microns, a region in which a capsule in space operating at a moderate temperature emits more than 99 percent of its excess heat energy.

Coatings in Temperature Control

Because of their versatility, low cost, and ease of application, organic coatings received early attention as a possible solution to this problem. Initially, two questions required immediate answers: (i) How long will properly designed organic coatings retain their properties (particularly their optical properties) in the space environment? (ii) What can be provided, in a variety of practical surface coatings possessing a wide range of absorptivity-to-emission ratios, to meet most design criteria? Much of the work accomplished in the past few years has been designed to provide answers to these questions.

To assume that relatively thin films of organic polymers would be stable in the unfiltered sunlight of space required considerable imagination initially. For decades paint technologists have evaluated their products by exposing them to the intense sunlight of southern latitudes and testing them in machines producing radiation enriched in the ultraviolet region. Thus, organic coatings have been developed which contain highly reflecting pigments to shield the organic matrix from attack by ultraviolet energy, and ultraviolet absorbers have been widely adopted which screen much of the harmful energy from the spectrum before it can be absorbed by the organic matrix. More recently, film-forming polymers have been designed which show a marked innate resistance to degradation by radiant energy. Thus, attention was focused early on the behavior of film-forming polymers exposed to intense ultraviolet energy in vacuum systems.

The intensity of sunlight reaching the earth's outer atmosphere is about 2 calories per square centimeter per minute; approximately 9 percent of this energy is in the region between 2000 and 4000 Å (4). Tousey (5) has, by means of probes, measured the spectral distribution of ultraviolet light above the atmosphere; Table 1 shows the

The author is head of the Organic and Biological Chemistry Branch of the Chemistry Division, U.S. Naval Research Laboratory, Washington, D.C.

fraction of solar energy in the spectrum below the wavelengths indicated.

Thus it is evident that there is approximately 1000 times as much solar energy emitted between 0.2 and 0.4 micron (the near-ultraviolet region) as below 0.2 micron (the far-ultraviolet region). While each photon of energy emitted below 0.2 micron is relatively harmful to organic materials, it is believed that the total amount of such energy is so small as to be less deleterious than the cumulative effects of the energy in the more intense nearultraviolet region. Moreover, a normal terrestrial atmosphere absorbs almost 100 percent of the ultraviolet energy below 3000 Å and significantly reduces the intensity of the portion of the spectrum above 3000 Å before the energy reaches the earth's surface. Thus, it was generally assumed that the deterioration of organic materials which is usually expected at the earth's surface might very well be accelerated outside the atmosphere. Results in the Naval Research Laboratory indicate that this need not be the case, and, indeed, evidence exists that some filmforming polymers are more stable in an airless and moistureless environment than they are in air. For example, organic films irradiated in air degrade in predictable fashion (6), and the mechanism of their decomposition may be followed in the infrared spectrometer. On the other hand, similar films irradiated in a vacuum show few, if any, changes detectable from infrared spectra, but certain other changes are noticeable, such as yellowing and an increase in brittleness and hardness, suggesting further polymerization or cross-linking, arising, very probably, from the formation and recombination of free radicals. Evidence exists that, in some instances of irradiation in a vacuum, free radicals may be formed which do not recombine immediately; when air is subsequently introduced into the system, reactions occur that result in some scission, which can be followed by means of infrared spectra and measurable weight losses.

Two additional factors must be considered in selecting materials for use in space. These are, (i) the extreme vacuum that may promote rapid volatilization of some organics, and (ii) the relatively wide extremes of temperature that may be encountered. It has been estimated (7) that the equilibrium temperature reached by a structure in space in an orbit 765 kilometers high is approximately 168°K for a highly Table 1. Distribution of solar energy at short wavelengths (see 5).

λ (Å)	Fraction of total solar energy below λ		
7000	0.5		
4000	.1		
3000	.01		
2400	.001		
1900	.0001		
1600	.00001		
1000	.000001		

polished surface possessing a low absorptivity and emissivity in the earth's shadow. The same body may reach 394°K when exposed to full sunlight. This equilibrium temperature, of course, may be raised or lowered by varying the absorptivity and emissivity of the surface. This maximum temperature is well within the tolerance of a number of film-forming polymers. On the other hand, most organic materials become quite brittle at the lower extreme, and perhaps in space the lower extremes of temperature will have a more specific effect on the life of an organic coating than the maximum temperature to be expected.

Current Research Trends

Since 1957 a great deal of attention has been given to the behavior of materials in space. While some data have been obtained by projecting probes and satellites into the actual environments of interest, the vast bulk of the information has been derived from laboratory equipment designed to emulate the environment outside the earth's atmosphere. Most common among the items of equipment are vacuum chambers into which materials of interest may be placed, which may be evacuated to pressures of 10⁻⁷ mm-Hg and sometimes lower. These chambers are equipped with ultraviolet radiation sources and instruments capable of measuring

Table	2.	The	no	rma	1 emissivities	of	typical
surface	e i	nateri	als	at	100°C.		

Sample*	Emis- sivity	
Black silicone paint	0.88	
White (zinc sulfide, 30% pigment, by volume) silicone paint	.77	
Clear (unpigmented) silicone var- nish	.74	
Anodized 24S-T aluminum (uncoated; chromic acid process) Aluminum (leafing pigment) silicone	.55	
paint	.33	
Black acrylic lacquer (control)	.90	
* All organic coatings are 2 mils thick,	on ano-	

dized aluminum.

the intensity of the energy actually striking the specimen under study. Further refinements may include thermocouples for temperature measurement, and quartz windows which will permit direct measurement of infrared absorption of gaseous decomposition products as well as of the samples themselves, in the case of some transparent materials (8-10).

Work in our laboratory has been directed along two lines. First, data of considerable practical significance have been needed to fulfill current and immediate design requirements for certain satellites (Vanguard, for example) and probes. Second, a more basic approach has been taken with a view to elucidating the mechanisms involved in the process of polymer degradation; these, in turn, should suggest means by which more inherently stable polymers might be tailored.

In the first approach a large number of organic coatings, both pigmented and clear, were studied to determine the stability of their optical and physical properties under exposure to simulated conditions of space. These experiments have been described in detail elsewhere (9) and are summarized here.

The photodegradation of thin films of many organic polymers is much less rapid in a vacuum than in a normal atmosphere, for a given amount of ultraviolet radiation. In the normal terrestrial atmosphere, containing oxygen and water vapor, the usually dominant photochemical reaction appears to result in scission of the polymer chain, whereas in a vacuum, cross-linking and perhaps further polymerization occurs. In many cases cross-linking can be accommodated until it becomes excessive. In such cases films become embrittled, they shrink, and they lose adhesion. Although not so destructive physically as scission, cross-linking should be controlled for ultimate stability of film properties. There is little question, however, that scission and cross-linking do occur simultaneously and, therefore, that the results observed are indicative of the predominant induced reaction in the environment in question.

In general, all the polymer films examined became very strong absorbers of ultraviolet energy after a few hours' exposure to experimental conditions. Some resins are inherently strong absorbers of ultraviolet energy under any circumstances, but in these experiments such materials as urea formaldehyde and methacrylate, normally considered

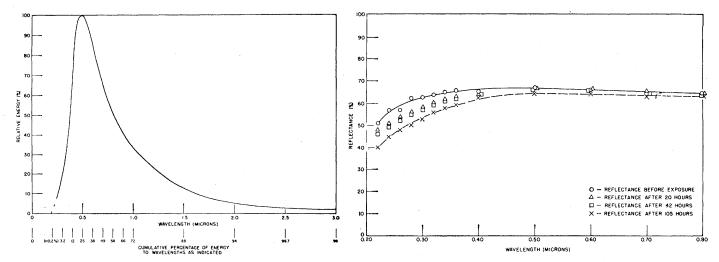


Fig. 1 (left). Approximate relative spectral distribution of solar energy outside the earth's atmosphere. Fig. 2 (right). Plot of reflectance of irradiated leafing aluminum flake in silicone resin. [From Noonan et al. (23)]

mild absorbers, became strong absorbers after a brief period of irradiation. Volatilization of unpigmented polymers during irradiation, as evinced by measurements of weight loss, varies widely between polymers but appears to be related to the opposing reactions of scission and cross-linking. Volatilization of silicone, melamine, and urea formaldehyde resins was slight-to-moderate in a normal atmosphere, while in a vacuum, weight loss in the silicone was negligible-a significant fact, which was a factor in the choice of silicones as a matrix for the carrier of the optically stable pigments selected for several satellites now in orbit.

As stated earlier, a most important objective of work in this area has been the production of a stable film possessing a low ratio of solar energy absorption α_* to infrared emission ε . Film discoloration resulting from ultraviolet radiation contributes to the difficulty. Thus, the problem can be narrowed to that of designing films possessing stable optical properties while maintaining a low α_*/ε value. Of course, the normal physical properties of the films must be maintained, but ultimate acceptability will depend on the possession of optical properties of required stability.

Optical Measurements

Values for hemispheric emittance (primarily infrared emittance) of materials of the type under consideration here are relatively difficult to obtain. Jakob (11) has published some interesting and pertinent relationships between normal emissivity and total emissivity (that is, hemispheric emissivity)

14 FEBRUARY 1964

for various surfaces. According to Jakob's relationships, the hemispheric emittance of a black silicone reference coating should be about 0.94 times its normal emittance. The normal emittance was found to be 0.88 for a 0.005-cm film at 100°C, relative to a cavity-type black body at the same temperature. Hence, the hemispheric, or total, emittance would be approximately 0.83, according to Jakob's relationships. The emissivity of this coating does not vary significantly over the temperature range 0° to 100°C. In Table 2 are listed the values for normal emittance of several typical coatings of interest.

Since the values for emissivity, ε , do not change drastically during irradiation, attention was focused on reflectance studies, with emphasis on optical stability. Total spectral reflectance was measured with a Beckman model DK-2 recording spectrophotometer equipped with an integrating sphere. In a few instances, changes in reflectance with time of irradiation are seen, and it is on the basis of these findings that optimum materials are chosen. In order to better understand these changes in reflectance, let us consider the relationship shown in Fig. 1, which shows the theoretical black-body emission spectrum of a 6000°K source which approximates the emission spectrum of the sun. Just below the abscissa the cumulative percentage of energy up to the designated wavelengths is indicated. It may be noted that the spectral reflectance of the materials under study was obtained over the range of 0.22 micron to 2.7 microns-a region in which approximately 97 percent of the sun's energy is emitted.

In Figs. 2, 3, and 4, changes in reflectance are shown for materials irradiated at ultraviolet wavelengths. In Fig. 2 it is evident that the reflectance of leafing aluminum flake dispersed in silicone is only mildly degraded by ultraviolet irradiation. Moreover, zinc sulfide similarly dispersed (Fig. 3) loses perceptibly more reflective power, but its reflectance remains quite high at the wavelengths of importance. On the other hand, basic white lead carbonate (Fig. 4) is degraded appreciably under the same conditions. Similar studies on a variety of materials have suggested that zinc sulfide dispersed in silicone resin is among the more stable materials for surface coating of vehicles in space. The small change in reflectance, coupled with the relative high emissivity, makes the combination a good one for this use. In fact, this is the formulation used for the thirdstage rocket of Vanguard I. Recently Zerlaut and Harada (12) published data that show high-purity zinc oxide to be as good as, or perhaps somewhat better than, zinc sulfide when dispersed in a silicone resin.

From numerous experiments of the kind described, a number of facts have emerged which have guided designers in the designation of coatings for the exteriors of spacecraft and satellites. Resins derived from acrylic acid absorb minimum amounts of the energy to which they are subjected. Silicones, on the other hand, absorb much ultraviolet energy, but their molecular structure is such that they are capable of absorbing and dissipating large amounts of this energy without suffering severe degradation. Somewhat paradoxically, the better silicone film-formers are the

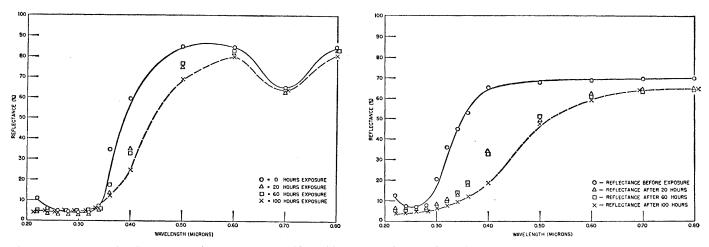


Fig. 3 (left). Plot of reflectance of irradiated zinc sulfide [30 percent pigment (by volume) in dry film, in silicone]. Fig. 4 (right). Plot of reflectance of irradiated basic white lead carbonate [30 percent pigment (by volume) in dry film, in silicone]. [From Noonan *et al.* (23)]

stronger absorbers of ultraviolet radiation, because of the presence of large numbers of phenyl groups in their structure. Methyl silicones are substantially transparent to ultraviolet energy, down to wavelengths of 2100 Å or less, and would provide excellent matrices for use in space, but rather unfortunately they are not among the best film-forming polymers. Finally, urea formaldehyde-butyrate is an excellent matrix, because of its low absorption of ultraviolet energy.

Studies of pigments have been somewhat less rewarding. An ideal pigment should have an extremely high refractive index in the ultraviolet. Conversely it should have low absorptance in the same frequencies or should be transparent. Even those pigments that display a fair degree of reflectance lose it during irradiation. Basic white lead carbonate, long used as the standard in outside white paints, becomes a very poor reflector of ultraviolet energy after brief exposure to this radiation (Fig. 4).

Polymer Photolysis

In the second phase of our work, Fox and his associates (13-15) synthesized several very pure polymers and studied their photolytic degradation with a view to gaining further understanding of the mechanisms involved. Such information should be useful in the design of polymers of enhanced stability. The photolytic degradation, in a vacuum, of $poly(\alpha$ -methylstyrene) was of interest, since a comparison could be made between the ultraviolet degradation in polymers containing the aromatic chromophore and the carbonyl chromophore of polymers such as poly(methyl isopropenyl ketone), which has been investigated by others (16). Such a study would also afford a comparison with the effects of ionizing radiation (17), as well as with degradation by thermal means (18), the mechanisms for which are well established.

In initial experiments (13), films of poly(α -methylstyrene) were cast on quartz plates. Ultraviolet absorption of

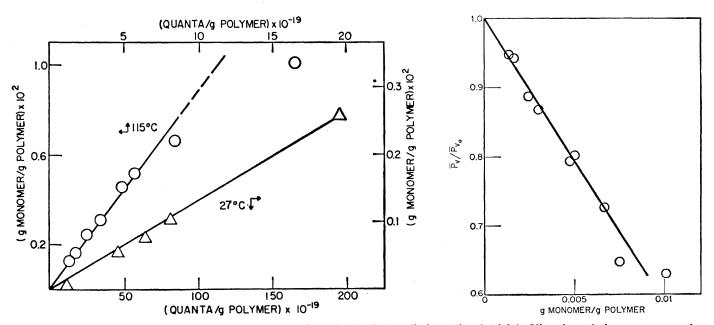


Fig. 5 (left). Plot of formation of monomer as a function of absorbed radiation. Fig. 6 (right). Viscosity relative to average degree of polymerization, plotted as a function of conversion to monomer at 115°C.

the film was measured; the plates were then placed in an irradiation cell, which was subsequently evacuated. The equipment was of such design that condensable products deriving from the irradiation could be collected and transferred to a low-temperature still, then fractionated and frozen into breakseal tubes for subsequent mass spectrometric analysis. Noncondensable gases were transferred to analysis tubes by a Toepler pump behind a mercury floodvalve cutoff. After irradiation the polymer was dissolved, precipitated, dried, weighed, and redissolved for viscosity measurement. The concentration of the monomer in the decantate from the first precipitation was determined from its absorption at 2430 Å. Identification of gaseous products was made by mass spectroscopy. Irradiations were made at temperatures of 27° and 115°C, respectively. With uranyl oxalate actinometry (19) the number of quanta absorbed by the films at the photochemically active wavelengths was determined, by the method of Jortner (20).

When poly(α -methylstyrene) is irradiated with ultraviolet light under the conditions outlined, small amounts of monomer are formed; their formation is accompanied by an immediate decrease in the molecular weight of the residual polymer. Monomer accounts for the largest proportion of non-polymeric degradation products. The results from a typical analysis are shown in Table 3.

The monomer formed as a function of the radiation absorbed is shown in Fig. 5 for irradiations at two temperatures. Thus, there appears to be a linear relation between the amount of monomer formed and the energy absorbed in the initial stages. As the reaction progresses, the concentration of monomer in the film increases and the amount of energy absorbed by the polymer per unit time decreases, due to overlapping of ultraviolet absorption bands of the monomer and polymer.

Intrinsic viscosity is an important index to degree of polymerization or molecular size. For a typical irradiation of poly(α -methylstyrene) at 115°C, the ratio [(viscosity of residue)/(average degree of polymerization of residue)] relative to the ratio [(initial viscosity)/ (initial average degree of polymerization)] is plotted in Fig. 6 against the weight fraction converted to monomer. A sharp decrease in the degree-of-polymerization ratio as compared to the

14 FEBRUARY 1964

Table 3. Volatile photodegradation products of poly(α -methylstyrene). In the mass spectroscopy, a trace of monomer was found in volatiles. Monomer in polymer residue, 85.1 $\times 10^{-7}$ mole; quantum yield, 0.34; irradiation temperature, 115°C; sample size, 0.09 g; einsteins absorbed, 2.5 $\times 10^{-5}$; \overline{P}_{ν} , 1140.

Products	Moles $(\times 10^7)$	Quantum yield
Hydrogen	4.2	0.017
ĊŎ,	4.0	.016
CO	1.7	.0068
Acetylene	0.7	.0028
Ethylene	.6	.0024
Isobutene	.5	.0020
Methane	.3 .3	.0012
Ethane	.3	.0012
Propene	.2	.0008
Butanes	.2	.0008
Branched pentanes	.1	.0004
Benzene	9.0	
Toluene	0.1	

fraction converted to monomer is indicated. Such a large decrease in molecular weight without concomitant formation of large amounts of monomer generally indicates a random breaking of bonds in the polymer backbone.

Stokes and Fox (13) explain these results in terms of Jellinek's theory (21) for the initial stages of degradation with random initiation and reverse polymerization. In this theory, the initiation reaction results in the random breaking of carbon bonds in the polymer chain, which in $poly(\alpha-methylsty-$ rene) is given by the structure of Fig. 7. The depolymerization reaction may be written as shown in Fig. 8.

The intensity exponent was found to be about 1.0 in our experiments, indicating that the termination is first-order with respect to polymer radicals. Since there is practically no diffusion of monomer from the film in the temperature range used, it is probable that polymer radicals terminate by transfer to monomer molecules (17), as shown in Fig. 9.

Similar and related studies have been completed recently (22) in which the photolysis of poly(methyl acrylate) in vacuum and in air was reported, and the photodegradation of poly(α -methylstyrene) in solution (15) has been investigated. In each instance additional evidence has been presented to explain further the mechanisms involved in the degradation of polymeric structures by ultraviolet energy.

Summary

The necessity for temperature control in orbiting satellites and in spacecraft has been recognized since the earliest launchings. Coatings, both organic and inorganic, offer interesting possibilities for maintaining passive thermal control. Moreover, films of organic polymers of reasonable stability under

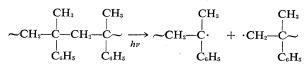


Fig. 7. Initiation of the degradation reaction in $poly(\alpha$ -methylstyrene).

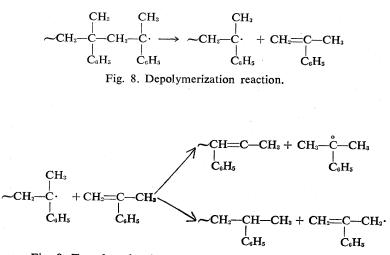


Fig. 9. Transfer of polymer radicals to monomer molecules.

659

ultraviolet irradiation and properly reinforced with pigments of optimum optical characteristics can be used to advantage. As a result of the studies reported, such polymers are available in the silicones and acrylates. Other investigations currently in progress may be expected to lead to the development of even more stable and efficient materials for controlling the reflectance and emissivity of bodies in space, and thus for controlling their temperature.

References and Notes

- 1. W. G. Camack and D. K. Edwards, in
- W. G. Callack and D. R. Dewind, In Surface Effects on Spacecraft Materials (Wiley, New York, 1960), p. 3.
 C. E. A. Winslow, in Temperature, Its Mea-surement and Control in Science and In-dustry (Reinhold, New York, 1941), vol. 1,
- *dustry* (Reinhold, New York, 1941), Vol. 1, p. 509. 3. P. E. Sandorff and J. S. Prigge, *Astronautics* **3**, 4 (1956); C. M. Schmidt and A. J. Hana-walt, *Jet Propulsion* **27**, 1079 (1957); E. P.

Buwalda and A. R. Hibbs, Jet Propulsion Laboratory, California Institute of Tech-nology External Publ. 481 (1958); L. Drumand M. Schach, in Rockets and Satelmeter lites, Annals of the International Geophysical Year, L. B. Berkner, Ed. (Pergamon, Lon-don, 1958), vol. 6, p. 304; K. Buettner, in *Physics and Medicine of the Upper At-mosphere*, C. S. White and O. Benson, Eds. (Univ. of New Mexico Press, Albuquerque, 1952), p. 89 1952), p. 88. F. S. Johnson, J. Meteorol. 11, 431 (1954).

- 1952), p. 88.
 F. S. Johnson, J. Meteorol. 11, 431 (1954).
 F. Tousey, Astronautics 6, 32 (July 1961).
 S. B. Crecelius, R. E. Kagarise, A. L. Alexander, Ind. Eng. Chem. 47, 1643 (1955).
 L. E. Gatzek and L. Isenberg, in "Materials Compatibility and Contamination Control Processes." Proc. Symposium Society of Aerospace Material and Process Engineers, St. Louis, 1962 (1963), p. 12.
 Several designs have been described in a number of Naval Research Laboratory publications: see 9 and 10.
- lications; see 9 and 10.
- 9. J. E. Cowling, A. L. Alexander, R. Kag-J. E. Cowling, A. L. Alexander, K. Kag-arise, S. Stokes, in Surface Effects on Space-craft Materials (Wiley, New York, 1960), p. 364; J. E. Cowling, D. E. Field, A. L. Alexander, Offic. Dig. Federation Soc. Paint Technol. 34, 816 (1962); D. E. Field, J. E. Cowling, F. M. Noonan, Naval Research Laboratory Rept. 5737 (Mar. 1962).
- News and Comment

Civilian Technology: Opposition in Congress and Industry Leads to Major Realignment of Program

When the Kennedy administration came into office, it let loose a gusher of proposals aimed at bringing new ideas, practices, and government money into numerous aspects of national life. Among these proposals, one of the most ambitious and imaginative was the Commerce Department's Civilian Industrial Technology (CIT) program, which was designed to stimulate American industry to partake more deeply of advanced science and technology. (Science 15 Feb., 28 June 1963.)

Industry, with a few exceptions, reacted adversely, contending that CIT would simply be taking taxes from successful industries to promote research aimed at building up faltering competitors. In unison with industrial lobbyists, Congress last year took up this theme and gave CIT one of the worst drubbings afforded any Kennedy proposal. Earlier this month, in what might be called a well-ordered retreat to previously prepared positions, the remnants of CIT fell back to the Commerce Department's National Bureau of Standards (NBS), where, the hope is, it will be able to regroup and prosper along lines less threatening to industry.

In line with this move, the CIT program itself is disappearing as an organizational entity; its various parts are to be distributed among four newly established groupings which will encompass all of the Bureau's activities. These are:

1) The Institute for Basic Standards. Under the directorship of Robert D. Huntoon, NBS Deputy Director for basic standards and services, it will handle all NBS programs of basic measurement standards, including the recently established National Standard Reference Data Program.

2) The Institute for Materials Research. With Earl C. Schoonover, Deputy Director for technological standards and services, as acting director, the institute will combine NBS programs in chemistry and metallurgy aimed at developing uniform material property measurements.

3) The Central Radio Propagation Laboratory at Boulder, Colorado. Headed by its present director, C. Gordon Little, the laboratory will continue its programs of services to government and industry.

- 10. C. G. Goetzel and John B. Singleterry, Eds., Space Materials Handbook (Lockheed Mis-siles and Space Co., Sunnyvale, Calif., 1962).
- siles and Space Co., Sunnyvale, Calif., 1962).
 M. Jakob, Heat Transfer (Wiley, New York, 1949), vol. 1.
 G. A. Zerlaut and Y. Harada, Research Institute Technology Center, Chicago, Rept. 11TR1-C207-25, IIT (1963).
 S. Stokes and R. Fox, J. Polymer Sci. 56, 507 (1962).
- 14. R. Fox, L. Isaacs, S. Stokes, ibid. 1A, 1079
- (1963). 15. R. Fox,
- , Am. Chem. Soc. (News Ed.) 23, 213 (1963). No. 2, 213 (1963). K. F. Wissbrun, J. Am. Chem. Soc. 81, 58 16. K
- (1959) 17. A. M. (1959). M. Kotliar, J. Appl. Polymer Sci. 2, 134
- (1959).
 18. D. W. Brown and L. A. Wall, J. Phys. Chem.
 62, 848 (1958); D. H. Grant, E. Vance, S. Bywater, Trans. Faraday Soc. 56, 1697 (1960).
 19. G. S. Forbes and L. J. Heidt, J. Am. Chem. Soc. 56, 2363 (1934).
 20. J. Jortner, J. Polymer Sci. 37, 199 (1959).
 21. H. H. G. Jellinek, Degradation of Vinyl Polymers (Academic, New York, 1955), p. 51.
 22. R. Fox, L. Isaacs, S. Stokes, R. Kagarise, J. Polymer Sci., in press.
 23. F. M. Noonan, A. L. Alexander, J. E. Cowling, Naval Research Laboratory Rept. 5503 (1960).

ling, N (1960).

4) Institute of Applied Technology. Headed by Donald A. Schon, an Arthur D. Little, Inc., staff member who joined the Commerce Department to head its Office of Technical Services (OTS), the institute will inherit the principal remnant of CIT, a \$1-million textile research program, which was the only part of CIT to receive congressional approval. In addition, the institute will handle the OTS technical information programs, designed to provide industry with information on new processes and techniques, and it will be in charge of a variety of other NBS activities related to industrial innovations.

Meanwhile, at the direction of Congress, the managers of the departed CIT program are now drafting legislation that would authorize one of the most cherished parts of their designa university-based extension service that would provide industry with technical counsel in much the same manner that the Agriculture Department's extension service aids the nation's farmers. Early in the game, there prevailed the hope that the Commerce Department had authority to carry out this activity without new legislation, but the Congress, in its antipathy to CIT, felt otherwise.

The defeat administered CIT has had no visible effect on the spirits of J. Herbert Holloman, the Commerce Department Assistant Secretary for Science and Technology, who was the key man behind the original program and who is behind its current regrouping. Numerous persons associated with or interested in CIT are now proclaiming that, if Holloman had accepted their