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Solar Energy Collector Coatings from Cyclopolymers of Butadiene and Acrylonitrile

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Synopsis

Solar energy-absorbing coatings have been prepared from commercially available polymers of acrylonitrile and butadiene by coating films of these polymers on aluminum panels and heating them at 600°F. These coatings are more selective and, therefore, of higher theoretical efficiency than black paints presently used as solar thermal absorbers. Our results show that the selectivity of the absorber is a function of its thickness, and the optimum thickness is below 0.30 mils. This discovery opens a new line of possible research in the design of polymer films as solar energy absorbers.

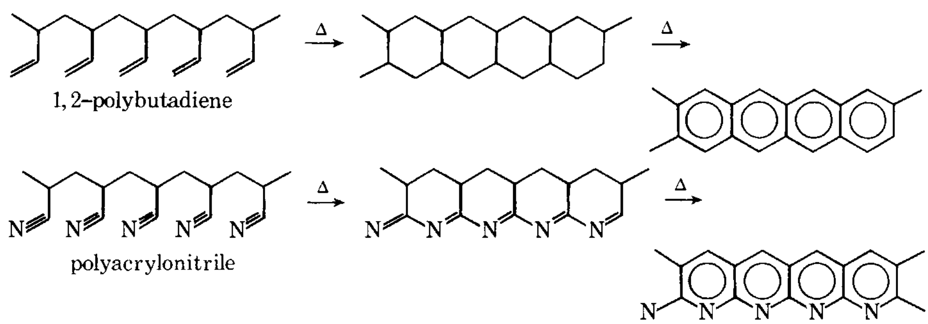
INTRODUCTION

Solar energy collectors are devices for absorbing solar energy and converting it into useful thermal energy. The absorbing surface of the collector may be coated with a flat black paint or may be produced by some other process which blackens the surface of metals such as copper, nickel, or chromium.[1] In order to trap as much of the incident radiation as possible, it is desirable to prepare an absorbing surface with an absorptance of 0.9 or greater in the spectral range of solar energy reaching the surface of the earth. The thermal energy which is produced in the collector is generally transferred by a circulating fluid from the collector to the site where it is used. This energy also raises the temperature of the collector and causes it to radiate energy. Because the maximum temperature of solar energy collectors does not generally exceed 300°C, the energy they radiate is in the infrared region of the spectrum with wavelengths of 3–15 microns. In general, therefore, an efficient solar collector is one which has a high absorptance in the visible and ultraviolet range of the spectrum and a low emittance in the infrared range.

Two general types of coatings have been described in the literature. One is called "selective" and the other, "nonselective." Selective coatings have high absorptances in the wavelength range of 1–3 microns and low emittance in the range of 3–15 microns. Nonselective coatings have both high absorptance and high emittance in the ranges discussed above.[2] In general, nonselective coatings are paints made by dispersing finely divided carbon such as carbon black or lamp black in a polymeric binder. These coatings generally have absorptances and emittances of about 0.9 each. Selective coatings on the other hand have absorptances of about 0.9 and emittances of about 0.1.[3] For the purpose of this study, we have defined a selectivity factor which is a measure of the efficiency of a coating as a solar energy absorber. This factor is obtained by dividing the absorptance (a) by the emittance (e). Nonselective coatings have values of a/e close to 1.0, while selective coatings have values of 9.0 and greater.

In this paper, we report the preparation of selective solar energy collectors from cyclopolymers of butadiene and acrylonitrile. These polymers were studied because, in addition to providing good optical properties, they have good thermal stability and can be prepared and applied easily. These properties make them more desirable than the alkyd binders used in commercial paints.

Gaylord and co-workers have shown that conjugated dienes can be polymerized to form ladder polymers consisting of long chains of fused rings.[4,5,6] The insoluble products have higher densities than polybutadiene and exhibit high thermal stability. Polyacrylonitrile has been pyrolized at temperatures in the range of 200–300°C to give a substance which darkens proportionately with the disappearance of the nitrile group.[7] The black product is insoluble in all solvents tested and exhibits superior heat stability. It has been suggested that the color-producing mechanism involves the formation of ladder polymers containing conjugated double bonds as shown below for 1,2-polybutadiene and polyacrylonitrile, respectively:[8]



This study was undertaken to determine whether the dark, thermally stable polymers produced on heating polyacrylonitrile and polybutadiene could be used in the preparation of solar energy-absorbing coatings. The objective was to test whether thin films of these polymers coated on metal surfaces could be heated to give the optical properties needed for solar energy absorbers. If the desired absorptance could be obtained, several steps in the presently used processes such as the preparation, milling, and dispersion of the pigments could be eliminated. This method also has some novel possibilities which are of theoretical interest in the design of solar energy-absorbing coatings. The minimum coating thickness which could be obtained from a pigmented paint is limited by the particle size of the pigment. No such limitation is envisioned for coatings prepared from a polymer solution, and it should be possible to prepare and study thinner and more uniform films than those which have been discussed in the literature before. It was decided that an important part of this study would be an examination of the effect of thickness on the optical properties of these coatings.

EXPERIMENTAL

Type 1100 aluminum panels, 4 in. × 6 in. × 0.060 in., were cleaned and coated by slowly pouring solutions of polyacrylonitrile and polybutadiene over them. The panels were allowed to air dry and were then heated in a oven with circulating air. Optical properties were determined at the Marshal Space Flight Center in Alabama. A Gier–Dunkle solar reflectometer was used to measure the absorptance, and the emittance was measured on the DB-100 infrared reflectometer. Coating thicknesses were determined with a Dermatron electronic thickness gauge. The polymers used were commercially available under the following trade names:

Poly-1,2-butadiene: Dienite PD-703, available from the Firestone Synthetic Rubber and Latex Company. Poly(1,2-butadiene–co–1,4-butadiene): Lithene AH, available from the Lithium Corporation of America. Poly(acrylonitrile–co–butadiene: Hycar CTBNX, available from the B. F. Goodrich Chemical Company. Polyacrylonitrile: PAN-601, available from Gumbs Associates.

RESULTS

When films of polyacrylonitrile on aluminum panels were heated for a half-hour at 650°F, they darkened to give optical properties that would make them useful as solar energy absorbers. Further heating did not show any change in these optical properties. The results are shown in Table I.

Films of different thicknesses ranging from 0.02 to 0.62 mils were prepared on aluminum panels, heated for 0.5 hr at 650°F, and their optical properties determined. The results are shown in Table II. The data show that the limiting absorptance is reached in a film of approximately 0.30 mil. As the film thickness is decreased from this value, the absorptance changes much more slowly than the emittance. Thus, in going to a film of thickness 0.02 mil, the absorptance changes by 0.17 for a corresponding chanee in the emittance of 0.51.

TABLE I
Optical Properties of Polyacrylonitrile (PAN-601) Coatings as a Function of Heating Time at 650°F

Film thickness, mils	Absorptance	Emittance	Heating time, hr
0.06	0.72	0.45	0.5
0.06	0.71	0.45	5.0

TABLE II
Optical Properties of Polyacrylonitrile (PAN-601) Coatings as a Function of Film Thickness

Film thickness, mils	Absorptance	Emittance
0.62	0.86	0.72
0.46	0.86	0.72
0.30	0.86	0.72
0.20	0.84	0.67
0.06	0.71	0.45
0.02	0.69	0.21

TABLE III
Optical Properties of Polybutadiene Coatings as a Function of Heating Time

Polymer	Heating time, hr	Absorptance	Emittance
Polybutadiene (Lithene AH)	2	0.73	0.72
Polybutadiene (Lithene AH)	4.5	0.77	0.74
Polybutadiene (Dienite PD-703)	1.8	0.76	0.72
Polybutadiene (Dienite PD-703)	1.8	0.76	0.68
Poly(acrylonitrile–co–butadiene) (Hycar CTBNX)	2.0	0.79	0.53[a]
	4.5	0.72	0.52

[a] This sample was heated at 650°F.

TABLE IV
The Ratio of Absorptance to Emittance (a/e) as a Function of Film Thickness of Polyacrylonitrile Coatings

Film thickness, mils	a/e
0.30	1.2
0.20	1.3
0.06	1.6
0.02	3.3

When films of polybutadiene were coated on aluminum panels and heated at 600°F, they darkened somewhat more slowly than the polyacrylonitrile films but gave coatings with generally similar optical properties. The films listed in Table III all had thicknesses greater than 0.30 mil.

DISCUSSION

The results shown in Tables I, II, and III clearly indicate that it is feasible to prepare solar energy-absorbing coatings by heating thin films of these selected polymers on metal surfaces. The limiting absorptance given in these tables are somewhat lower than the values reported in the literature for pigmented black paints.[3] The absorptances claimed for these absorbers are generally in the range of 0.90–0.95. As pointed out in our earlier introduction, the efficiency of an absorber is a function of both absorptance and emittance and is expected to correlate to a/e. Values of a/e for all the coatings we have reported are above the value of 1.0 calculated for pigmented black paints. This indicates a higher theoretical efficiency for our coatings.

Further, from the data in Table II, a/e values as a function of coating thickness may be determined. These are shown in Table IV. It can be seen that these values increase dramatically as the coating thickness is decreased. We do not know whether this is true for all types of polymer films, but there are good grounds for speculating that it might be. In fact, additional work in progress in our laboratories indicates that some polymer films with very low levels of carbon black show a similar dependence. Since emittance is a function of temperature, it might be expected that thick films which are poor thermal conductors would remain at a higher temperature than thin films of the same substance. Under these circumstances, decreasing film thickness would increase the rate of heat transfer to the metal support and would, thereby, reduce the amount of energy emitted as infrared radiation.

The most highly selective coatings which have been reported in the literature to date are "Black Chrome," "Black Nickel," and "Black Zinc." These are produced by expensive electroplating techniques and, although quite stable at high temperatures, are readily destroyed by moisture, salt sprays, and dilute acids. These coatings have a/e values of 9.0, with absorptances of 0.9; and it is possible that they have high selectivities simply because they are thin. Unfortunately, we have not been able to find published data on the thickness of these coatings. The results of this study, however, indicate that it is possible to make selective solar absorbers from inexpensive polymers by controlling the thickness of the absorbing layer.

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