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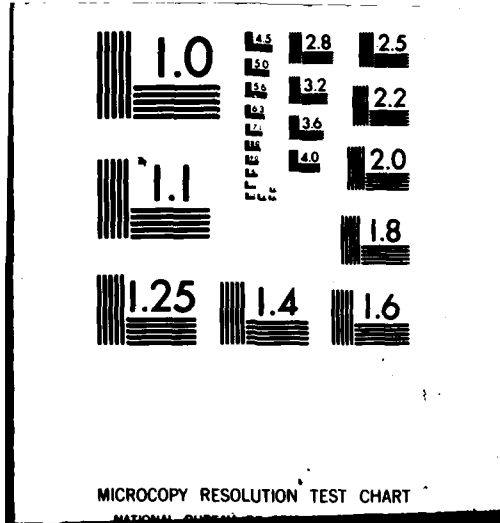
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**A METHOD OF POLYMER DESIGN AND SYNTHESIS FOR
SELECTIVE INFRARED ENERGY ABSORPTION**

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INTRODUCTION

Infrared-absorption spectroscopy is extensively used in polymer chemistry in the study of reaction processes, structure, morphology, qualitative and quantitative composition, molecular configuration, and other features. The rapid growth of the technique since the mid-1940's attests to its usefulness.

In the method, electromagnetic radiation in the infrared region (greater than $\lambda = 0.7 \mu\text{m}$) interacts with mass in vibrational and rotational modes. The interactions with molecules or groups of atoms within molecules causes transitions between the vibrational and/or rotational states with a resulting characteristic absorption of energy or spectral "signature." The spectrum produced relates the intensity of energy absorption at particular wavelengths by specific groups of atoms and provides an insight into the structure and configuration by providing both the types of groups and their concentrations. Infrared-absorption spectroscopy may be used alone as an analytical method; however, it is often combined with Raman and mass spectroscopy or with nuclear magnetic resonance to obtain more detailed information.

The present study presents a procedural method of designing and synthesizing polymers intended to selectively absorb energy in particular bands of the infrared spectrum. Thus, filters may be prepared that can be used to mask or alter the signatures of infrared-emitting objects and, in effect, camouflage these objects against observation by attenuating or altering the infrared energy that is allowed to be transmitted to a detector.

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In addition to the molecular design of the polymer, a change in the physical form by foaming is studied to determine this effect on the overall efficiency of the attenuating properties of the filter. An advantage of foaming the polymer is the ability to make essentially self-supporting filter enclosures for infrared emitters. The most obvious uses of selectively absorbing infrared filters are in military camouflaging applications and as photographic filters analogous to the visible light filters commonly used.

THEORETICAL

Infrared radiation energy causes only the vibrational and rotational energy state transitions described earlier; it is incapable of causing electron energy level changes. The transitions effected cause the molecules to react as a vibrating system of springs and masses that can be reasonably approximated as a simple harmonic system which can be analyzed by quantum mechanics techniques such as the Schrodinger wave equation with the condition

$$\nu = \frac{E_2 - E_1}{hc}$$

in which ν is the wave number, * E_1 and E_2 are discrete energy values of the two transition states, h is Planck's constant, and c is the velocity of light. Only vibrations resulting in changes in dipole moments cause infrared absorptions of a fundamental nature; overtone and combination vibrations may occur, but their intensities are generally much lower. The intensity of absorption is proportional to the square of the magnitude of the changing dipole moment in the vibration or rotation.

*The wave number is conventionally defined as $10^4/\lambda$ where λ is between 1 and 500 μ m; it allows better numerical description than does the wavelength λ .

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The number of possible vibrations in a polymer system containing N atoms is $3N$ wave numbers. Of these, six values represent whole molecule vibration or rotation transitions so the total number of possible absorptions becomes $3N-6$ in most cases. Not all vibrations are detectable in the infrared spectrum due to a lack of proper response by the molecule or group to the infrared energy or to precedent Raman (electrical polarizability) activity or molecular symmetry. It is possible to calculate all of the individual values for all of the vibration frequencies from atomic masses and geometric positions (chemical bond lengths and bond angles) and the force constants of the bonds if some of the values are independently provided from other sources such as mass spectroscopy and nuclear magnetic resonance.

The translations of vibrational or rotational energy via mass displacement occur as bond stretching (symmetric and asymmetric), deformation (symmetric bending), wagging, twisting, and rocking as defined and illustrated by Bikales [1]. In relatively simple polymer molecules such as polyethylene, the motions are well defined. More complex molecules, especially network or crosslinked polymers with a large number of different types of groups, present much more formidable problems of exact analytical description. Nearest neighbor interactions, hydrogen bonding, van der Waals forces, residual strain, and steric hindrances all may cause shifting of the absorption band in the spectrum, broadening of the band, or combination with other nearby bands with a concomitant alteration of the absorption intensity.

The amount of infrared energy that is absorbed (converse of transmitted) as an infrared beam is passed through a material depends linearly upon the incident radiation intensity and non-linearly upon the number of absorbing molecules or groups in the path. The functional relationship is given by the Beer-Lambert law [2] in which logarithms are required to give the correct quantitative value of absorption. Since the effect of the logarithm is less pronounced when weak absorption occurs, the difference in peak absorption can be used to describe the number of absorbing molecules or groups. The reverse is not true, however, since strong absorption results in very large changes in the logarithmic value of transmission, and care must be exercised in interpreting the results quantitatively in terms of the number of functional absorbing groups in the light path.

Given that each polymer group has characteristic absorption properties, it is then theoretically possible to select groups by type and quantity and to synthesize polymers such that absorption will occur at specific bands in the spectrum. As a result, infrared radiation incident on one side of a layer of such a material can be absorbed as it passes

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through the material with the shape and/or overall transmitted spectrum intensity significantly tailored to suit a desired result.

Relatively little work has been reported on the intentional design of polymers to absorb infrared energy over a substantial portion of the near and intermediate portions of the spectrum. Exceptions include long- and short-pass and interference filters designed principally for use in the study of the infrared spectrum itself [3].

EXPERIMENTAL

The experimental procedure used was selected to satisfy three objectives. First, a polymer system was selected to afford as much flexibility in design as practical. Second, the designed polymer was synthesized. Third, the infrared-absorption spectrum of the polymer was studied with the polymer as a film and as varying thicknesses of foam to determine whether the polymer absorbed as designed and to compare the performance of the film and the foam.

Polymer groups were cataloged with respect to their infrared absorption bands. The selected groups and references are given in Table 1. The groups, their vibrational modes and principal absorption bands are listed in Table 2. These tables do not cover the entire range of possibilities, but rather reflect a selection sufficiently broad to cover a reasonable portion of the infrared spectrum from wave number 4000 cm^{-1} to about wave number 700 cm^{-1} . More than 100,000 infrared spectra are available for comparison reference of polymer group absorption in the ASTM and Sadtler collections [2].

An examination of the composition of numerous polymers showed that the polyurethane family offered a great number of opportunities for inclusion of many of the desired groups. (As a contrast, polyethylene contains only CH_2 groups with no possibility of other groups other than CH_3 at the chain ends.) Furthermore, the polyurethanes are generally readily synthesized as both films and foams by using commercially available isocyanates and a wide variety of reactants that contain ether C-O, ester $-\text{C}(=\text{O})-\text{O}$, phosphate PO_4^{-3} , amine NH , amide $-\text{C}(=\text{O})-\text{NH}_2$, sulfur S-H, halogen C-X, silicon Si-H, Si-C, Si-O, and other groups. The general absorption assignments of the various groups are given in Table 2. As can be seen, these groups cover the entire spectrum from about 3600 cm^{-1} to 700 cm^{-1} wave numbers.

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The polyurethane was formulated using a polymethylenepolyphenylisocyanate and polyether polyol. The chemistry and reactions are described in [4]. Thin films of the formulated polyurethane were cast on a Teflon slab. Low-density foams were made of the same formulation but by necessity, the foams also contained silicone surfactant and monofluorotrichloromethane as a cell control and foaming agent, respectively. The foam was sliced into thin sheets of various thicknesses prior to testing.

Transmission spectra of the specimens were made on a Perkin-Elmer Infrared Spectrometer, Model 283B. The transmission method was selected over other techniques such as attenuated total reflectance or as particles dispersed and consolidated in potassium bromide pellets as described by Bikales [1]. The transmission mode represents the anticipated use as a filter and was thus considered the most appropriate test procedure. Comparable absorption spectra were obtained for the film and foam specimens; thus, the method appeared satisfactory.

EXPERIMENTAL RESULTS

A composite spectrograph of the film and foam specimens is shown as Figure 1. Curve 1 at the top of the graph is the transmission spectrum of a thin film (0.0178 mm) of the polyurethane polymer. Absorption peaks (which appear as valleys in the curve) are strong at numerous wave numbers, especially at about 1075 cm^{-1} , 1220 cm^{-1} , 1525 cm^{-1} , 1710 cm^{-1} , 2900 cm^{-1} , and 3300 cm^{-1} . The presumed absorbing groups are identified in the upper margin. Curves 2 through 5 are increasingly greater thicknesses of foam (0.0218 mm through 0.0533 mm) of the same polymer and, as can be seen, they retain the same general absorption features as the film, but the absorption peaks become less pronounced as the thickness increases and more total absorption occurs. A sufficiently thick specimen would totally block transmission and the whole spectrum would be absent, just as no specimen in the beam would allow complete transmission.

The somewhat erratic trace of the curves is probably due to reflective scattering of the beam; small deviations in the curve are not satisfactory for assignment of absorption groups or indicative of the dipole activity required for infrared absorption. These small deviations should be considered as artifacts of the test or ignored completely for the purposes of this paper.

A single experiment was conducted under field conditions to verify findings in the laboratory. The experiment compared the observability of two operating 60-kW diesel drives generator sets; one set was enclosed by sheets of polyurethane foam approximately 50 mm thick, and the other set

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was bare. The enclosed set was shielded along the sides and over the top only so as to not interfere with either cooling air flow from end to end or exhaust gas emission.

The test was conducted for a 26-hour period to include a complete solar day. Temperature measurements were made at various points on the skin of the unenclosed set and at corresponding geometric points on the enclosed set and its shield. Background temperatures of soil, vegetation, and air were also measured.

Analysis of the thermographs thus assembled showed a sharp contrast between the thermal profile of the bare set and the background, whereas the thermal profile of the surface of the foam enclosure was practically identical with the background. Thus, the enclosure effectively filtered or masked the thermal output from the generator and would prevent observation from directions other than directly at the unenclosed ends.

DISCUSSION

The multiple absorption peaks shown in Figure 1 are the result of the variety of different groups present in the polyurethane polymer. In addition to the prominent peaks described, many smaller peaks are evident. The overall absorption spectrum is essentially the form that was desired and could effectively filter an emission spectrum of an infrared source.

The foam specimens absorbed more than the equivalent solid film, as shown in Table 3. The increased absorption is attributed to substantial scattering caused by the large number of angles described by cell walls in the foam. Incidence of the beam with the cell walls increases reflection to the sides and backward.

The results of this study support the hypothesis that selectively absorbent polymers can be designed and made. Foamed polymer appears to be superior to a film of the same material of the same thickness when used as a filter for infrared radiation. It is believed that effective masking filters for emitters could be made to a particular specification to absorb much of the infrared spectrum within the range described in this paper.

While it was not a part of this study, it is known that colorants, dyes, pigments, and fillers can also be incorporated into a polymer (film or foam) to further alter the absorption properties.

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Field utility of foamed polymers was deemed feasible based on the results of the single experiment described. Obviously, more study will be required to design an optimum system for general application.

SUMMARY

A method of designing a polymer to be selectively absorbing in the infrared electromagnetic spectrum was studied. The design was intended to give as much absorption as possible in the region of 4000 cm^{-1} to 700 cm^{-1} wave numbers. A polyurethane polymer was synthesized which showed absorption in this range with numerous fairly prominent absorption peaks. Foam made of this polymer showed the same absorption characteristics but appeared to be more efficient as a total filter for the whole range, particularly at a thickness of about 1.9 mm or greater.

A field experiment showed promise for effectively camouflaging thermal sources such as operating generator sets by enclosing them with polyurethane foam sheets.

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Table 1
List of Groups of Interest and Applicable References

Group	References
- I	5,6,7,15,26,28,29
Ca-2	5,6,7,15,18,20,22,23,24,25,26,27
Ca-3	5,6,7,11,15,18,19,20,21
C-X (X = halogen)	5,41,42
C-C	5,36
C-C (aromatic)	5,6,7,37
C-C	5,6
C-C	5
C-H	5,6,8,35
C-H	5
NR	5,6,7,8,10,15,33
NR2	5,6,7,15,31,32
C-O	5,6,8,34
C=O	5,6,7,8,10
OH	6,7,10,15,34
P-H	6,45
PO ₃ ⁻³	6
PO ₄	6
P=O	5,45
Si-H	6,38
Si-O	6,39,40
Si-C	6,40
Si-X	6,40
SO ₂	6
SO ₃	6
C-S	6,44
ONO ₂ , NO ₃ ⁻¹	5,6,43

and Absorption Bands

Group	Association	Stretching, cm^{-1}	Deformation, cm^{-1}	Wagging, cm^{-1}
C-H	Aliphatic aromatic	2880-2900 (w) 3030 (w m)	1315-1350 (w) 700-900 (s) out-of-plane 100-1300 (m) in-plane	
	alkynes alkenes	3267-3340 (s) 3000-3030 (m)	610-680 (s) trans 965 990 (s) out-of-plane cis 650 730 (m) trans 1285-1300 (m) in-plane cis 1395-1430 (m) in-plane 1200-1215 intensifies 1400	
CH ₂	Halogen carbon carbonyl esters, Amides	3000 2900-2930		
		2916-2936 (s) asym 2843-2863 (m) sym	1450-1475 (m)	
CH ₃	Aliphatic Aromatics	2952-2972 (s) asym 2862-2882 (m) sym 2920-2930 (m) asym 2860-2870 (m) sym	1450-1475 (m) asym 1370-1380 (m) sym	
		1000-1400 (vs) 650-730 (m to s)		
C-F		510-700		
C-Cl		465-600		
C-Br		1140-1250 (s)		
C-I		1440-1625 (w m)	ring stretching	
C-C		1638-1692 (w m)		
C=C		2100-2260 (m w) depending on substitution		
C-N	Amines, aliphatic aromatic amide primary secondary	1032-1090 (m) asym 1250-1360 (s) asym 1310-1430 (w)		
		1270 (s) as Amide III	1515-1570 (s)	
C=O	Alkyl Aryl	2240-2260 (s) 2220-2240 (s)		

Table 2 (Cont'd)

N-H	Secondary amines Secondary amines Urethanes	3310-3360 (w) 3140-3480 (m) 3250-3340 (m)	1550-1650 (w) 1200-1305 (m) 1200-1305 (m)	Amine III	700-750 (m) 700-740 (m) 700-740 (m)
NH ²	Amines Amides	3330-3400 (w) 3350 (m)	1575-1660 (m) 1620-1650 (s)		750-850 (s) 600-750 (s)
C-O	Ethers, alkyl aromatic alkyl/aryl vinyl	1060-1150 (vs) 1230-1270 (vs) 1010 1050 (s) 1200-1225 (s) 1160-1210 (s) 1230-1260 (s) asym			
	Esters Acetate	1035-1060 (s) asym 1240-1280 1211-1248 1205-1221			
	Caronates, alkyl/alkyl alkyl/aryl aryl/aryl				
C=O	Amides, ureas, urethanes, carbon acids, carbonates, etc.	1600-1700 (s)			600-700
OH	Alcohols Carboxy acids Phenols	3300 (s) 3000 (s) 3200-3250	1260-1350 (s) 875-960 (m) 1211-1320 (s) 1180-1260 (s)		1260-1350 (s)
P-H		2275-2320 (m)	1080-1090 (m)		910-940 (m)
PO ₄ ⁻³		1000-1100 (s)			
P=O		1110-1250			
Si-H		2100-2250 (m)	800-950 (m)		800-845 (m)
Si-O	Siloxanes (open-chain) Alkoxy Silanols	1024-1055 (s) 1076-1095 (s) 1100 (m) 830-910 (s)			
Si-C	Methyl siloxanes Si-phenyl	660-850 (m) 1100-1125 (s)			
Si-X	(X = Halogen)	820-945 (s)			
SO ₄ ⁻²		1080-1125 (s) asym			
C-S	Aliphatic Aromatic	570-705 (m w) 1090			

Table 2 (Cont'd)

		1270-1285 (n) Sym	745-760 (m) 690-710 (m)
ONO_2	Nitro		
NO_3^-	Nitrate	1350-1380 (n) 815-835 (m)	

Table 3

Equivalent Solid Film/Foam Thickness and Relative Absorption at 3000 cm^{-1}

Foam Thickness, mm	Film Thickness Equivalent, mm	% Absorption
0.61	0.0178*	16.5*
0.76	0.0218	40
1.04	0.0305	75
1.50	0.0432	90
1.91	0.0533*	96*

*It is readily apparent that a three-fold increase in equivalent thickness causes almost a six-fold increase in absorption at this wave number. Essentially, the same ratio occurs all along the spectrum of 4000 cm^{-1} to 700 cm^{-1} .

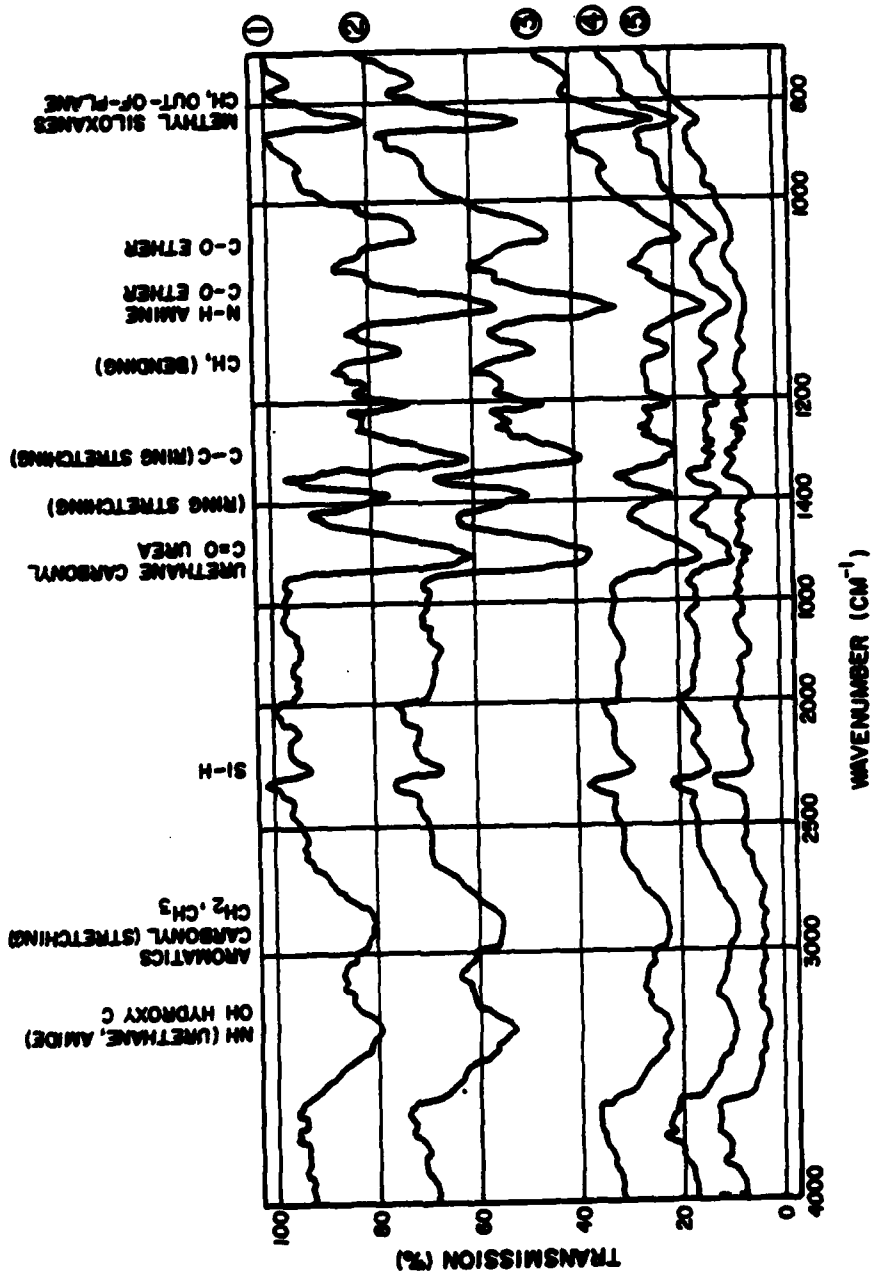


Figure 1. Comparison of Polyurethane Film and Foam Absorption Spectra