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SOLID PROPELLANT INGREDIENT MIGRATION STUDIES

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JUNE 1982

Final Report for the Period January 1980 Through December 1982

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Reported herein is the development of a unique solid propellant ingredient separation device. Use of this separation device was applied to the determination of labile solid propellant ingredient migration rates, propellant/liner plasticizer distribution ratio, and complete solid propellant ingredient analysis.

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Migration data are reported for numerous labile ingredients in both normal and min-smoke formulations. Di-n-octyl Phthalate distribution between carbon-filled liner and an AP/Al containing propellant was studied. "Balanced" liners were shown to exhibit significant plasticiser migration under the test conditions reported.

A sequential solvent extraction scheme is described wherein plasticiser, stabilizer, burnrate catalyst, RDX, HMX, AP, and Al can be accurately determined using less than 100 milligrams of cured propellant.

PREFACE

The objectives of AFRPL Project Number 573005RE, Task III were to determine the migration rates of selected solid propellant labile ingredients and to develop a means of predicting propellant/liner distributions of labile ingredients.

Techniques for experimental measurement of both migration rate and distribution of labile ingredients were developed and numerous migration rates were determined. It was discovered during the course of this experimental effort that migration rates are controlled by a number of extremely complex interrelated factors. Because of this complex behavior, the propellant/liner distribution of labile ingredients has defied prediction thus far.

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1. INTRODUCTION

Solid rocket motor performance requirements have become increasingly stringent. Not only are these requirements necessary when the motor is manufactured, but also little degradation is allowable even after many years of storage. There are many processes by which this complex mixture of ingredients can change which alter motor performance. Obviously, errors during the formulation process can cause the motor to fail even its initial qualifying tests. Although this failure is readily observed, to define the specific reason usually requires the use of complex analytical techniques. Slow decomposition of one or more of the ingredients with age may change solid rocket motor performance characteristics. As the demands for increased performance required more energetic ingredients, chemical reactivity problems became more common. Specifically adding other ingredients to the propellant mixture can often control the degree of reaction. The rate of consumption of these stabilizing ingredients is directly related to the age life of the motor; therefore, it is critical to accurately quantize these ingredients in the cured propellant. Even when undesirable post-cure reactions are controlled, liquid or dissolved solid ingredients (e.g., plasticizers, burn rate catalysts, and stabilizers) may migrate to or from parts of the motor such as the liner or insulation and slowly change the designed performance characteristics. Virtually all of the organizations involved in solid rocket motor technology are concerned with eliminating ingredient migration. Chemical bonding of these labile ingredients to the cross-linked binder is one method that has shown promise(1), but it may not be applicable to all migratable species in a formulation. Encapsulation of the grain, liner, and insulation with impervious materials is another method which is being studied extensively(2,3). Encapsulation can significantly affect the rate of ingredient transfer and considerable research is being directed toward improving the adhesion of these impervious layers to grains, insulations, and cases.

Many migration problems occur because the equilibrium distribution of a labile ingredient between the grain, liner, and insulation is not clearly defined. Normally it is assumed that when the concentrations of the ingredient are equal in the polymer portions of the grain, liner, and insulation, the motor is "balanced" and no migration can occur. This is often true provided no long-term thermal cycles occur and there are no other potentially interacting species such as carbon black, asbestos, and porous silica in the mixture. It seems reasonable to consider the various parts of a solid rocket motor to be similar to layers of viscous, impure, immiscible liquids. If this is true then prediction of labile ingredient distribution is very difficult. Studies to determine ingredient distribution must involve not only the actual formulations of materials but also should include temperature control. A thorough study may include determinations of ingredient distributions at several temperatures.

The development of any new solid rocket motor involves several years of micromotor tests and aging studies. In the aging studies samples of the formulated grain, liner, and insulation are stored under controlled temperature and humidity conditions, and periodically examined for changes in elongation, tensile strength, peel strength, and cross-linked binder content (sol/gel ratio). Frequently these tests can show that a change has occurred but they do little to define the specific cause. Normally to define the problem various motor ingredients are separated and quantitatively analyzed. Using conventional solvent extraction techniques requires relatively large samples and results in high solvent dilution which renders trace ingredients difficult to quantize. Often significant changes in propellant composition occur only at the layer interfaces and macro analysis techniques are inadequate to detect them. Recently a direct fourier transform infrared spectrometer (FTIR) examination method using an attenuated total reflectance (ATR) was developed (4). This technique requires only very small samples and virtually no sample preparation. It was found to be very useful for assessing changes in the cross-linked binder; however, quantization of labile ingredients was more difficult to do (5). Another micro examination technique specifically designed for labile ingredients uses a temperature-programmable, purged sample cell attached to a flame-ionization detector (6). Using this method to determine the quantity one or more ingredients is both rapid and accurate, but qualitative information is limited. Our early attempts to develop both a quantitative and qualitative micro separation technique for soluble ingredients resulted in somewhat less than quantitative recoveries. This research did establish that modern laboratory instrumentation could accurately analyze ingredients using only milligram quantities of solid propellant. This report describes a unique micro solvent extraction technique developed specifically to examine solid propellant layer interfaces which, when used with modern laboratory instrumentation, can provide accurate quantitative and qualitative information on all of the ingredients in a solid propellant formulation. It illustrates how to use this technique to determine migration rate and plasticizer distribution, and to determine each ingredient in the cured propellant grain.

2. EXPERIMENT

2.1 Rapid Analytical Propellant Extraction Device

Early experimental work in this laboratory established several critical requirements for an ingredient separation technique:

a. Maximum propellant sample thickness must be no more than 0.3 mm (0.01 in.) to accurately measure interface phenomena.

b. Extraction must occur in a nonequilibrium mode to be quantitative.

c. For required sensitivity, solvent accumulation must be minimal.

d. For selective ingredient separation, sequential solvent extraction on the sample is necessary.

The device pictured in Figure 1 met all of these requirements. The weighed sample, which was sandwiched between strips of a porous material (e.g., filter paper, glass fiber mat), was covered with a non-porous material (e.g., glass slides) to prevent solvent evaporation from the area near the sample. The exposed ends of the porous material were placed in a pure solvent and capillary action caused the solvent to pass over the sample and

(Patent Applied For)

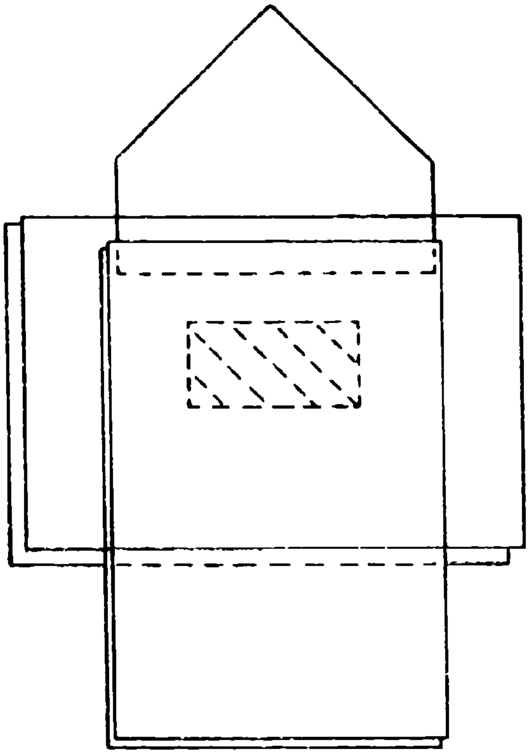


FIGURE 1, RAPID PROPELLANT EXTRACTION DEVICE evaporate from a third piece of porous material extending above the nonporous plates. The less volatile extract which remained on the third piece of porous material was redissolved in a known quantity of solvent and subjected to quantitative analysis. If a second solvent was required for additional ingredient extraction, then the upper porous strip was replaced with a fresh piece and the device was transferred to the next solvent of choice. When complete analysis was required this process was repeated using various solvents until only the cross-linked binder remained. In cases where elevated temperatures were required to increase solubility or reaction rate the device and solvent were placed in a vacuum oven maintained at ~600 mm Hg with a gaseous nitrogen purge. Two hours were normally sufficient for complete extraction of a particular ingredient.

2.2 Propellant Molds

Propellant and liner samples were prepared for migration and distribution coefficient studies using small polytetrafluorethylene molds shown in Figure 2. Relative migration rates were determined by placing an inert porous material saturated with the labile ingredient against the cured propellant and storing the assembly in an oven maintained at 60°C for several days or longer. After the migration period, the mold containing the propellant was sliced using a microtome. Once the depth (thickness) of each slice was determined, each slice was extracted and analyzed for labile ingredient content. Distribution coefficients were determined by first precuring a liner of known composition in one of the 1/8-in. thick molds; then by attaching propellant with a known composition (contained in a 1/4 in.-thick mold) to the liner with uncured liner from the same formulation. Whether the propellant was precured or uncured depended on the test requirements. The propellant/liner assembly was placed in an oven maintained at 60°C for several months; both the liner and propellant were sliced with a microtome; the depth of each slice determined; and each slice was subjected to extraction and analysis for the labile ingredient of interest. Generally, all slices analyzed were approximately 0.3 mm (0.01 in.) thick and the solvent used for the extraction was A.C.S. grade dichloromethane.

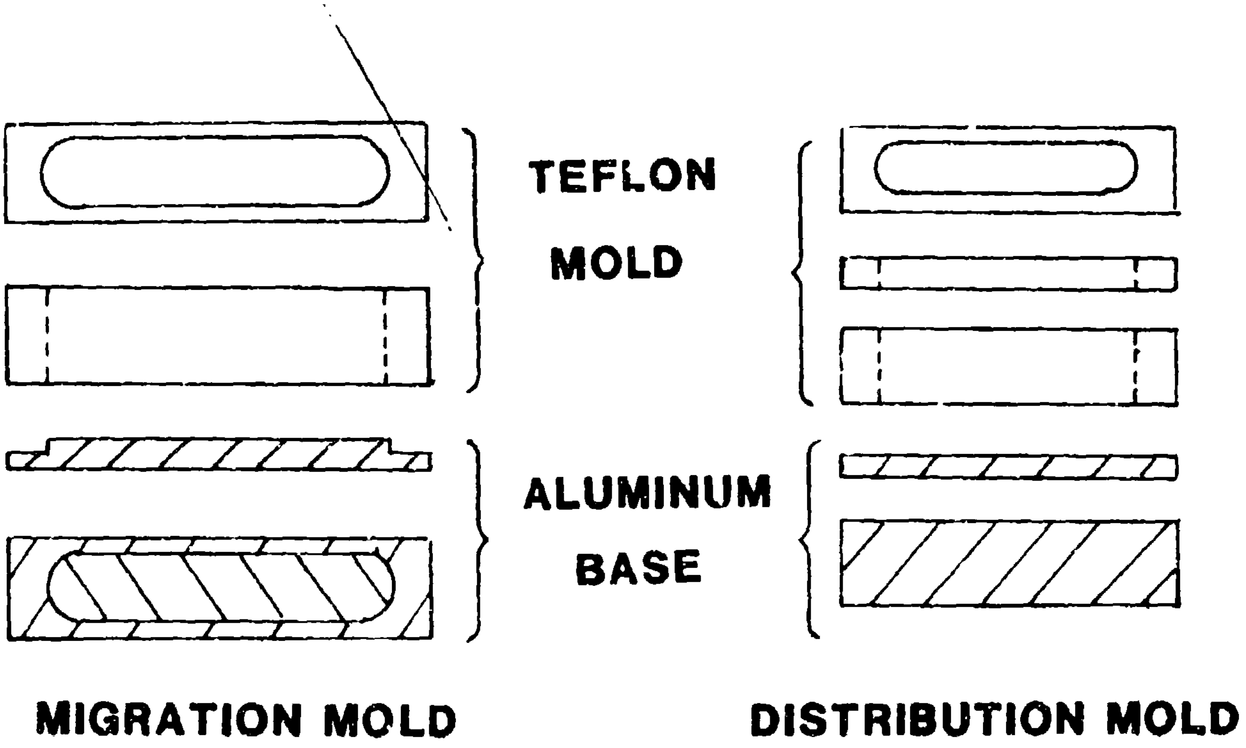


FIGURE 2, PROPELLANT MOLDS

2.3 Propellant Formulations

The migration rate of formulations which initially contained no plasticizer or other labile ingredients were studied. The following formulations are typical of those studied:

1. 20% HTPB/IPDI, 20% Al (27μ), 60% AP (50μ)
2. 28% R-18/IPDI, 72% HMX (57μ, 4μ)
3. 28% GAP/HDI, 72% HMX (57μ, 4μ)
4. 70% HTPB/IPDI, 30% Carbon Black (72 hr @ 80°C)

We used Formulations 1 and 4 for all plasticizer distribution experiments. Known quantities of di-n-octlyphthalate were included in the formulation and the distribution of this plasticizer between the propellant and liner was determined after aging. The carbon black used in the liner formulations was subjected to various pretreatments to assess its effect on the plasticizer distribution.

1. Normal - dried for 72 hr at 50 mm Hg and 80°C.
2. Wet - exposed to 90% R.H. for 21 days.
3. Dried - dried for 72 hr at 0.01 mm Hg and 160°C.
4. Extracted/Dried - extracted with CH_2Cl_2 for 72 hr, then dried for 72 hr at 0.01 mm Hg and 160°C.

The extract from Treatment 4, a yellow oil which was 2.6 percent of the total weight, appeared to be an impure aliphatic ester. The infrared spectrum is shown in Figure 3.

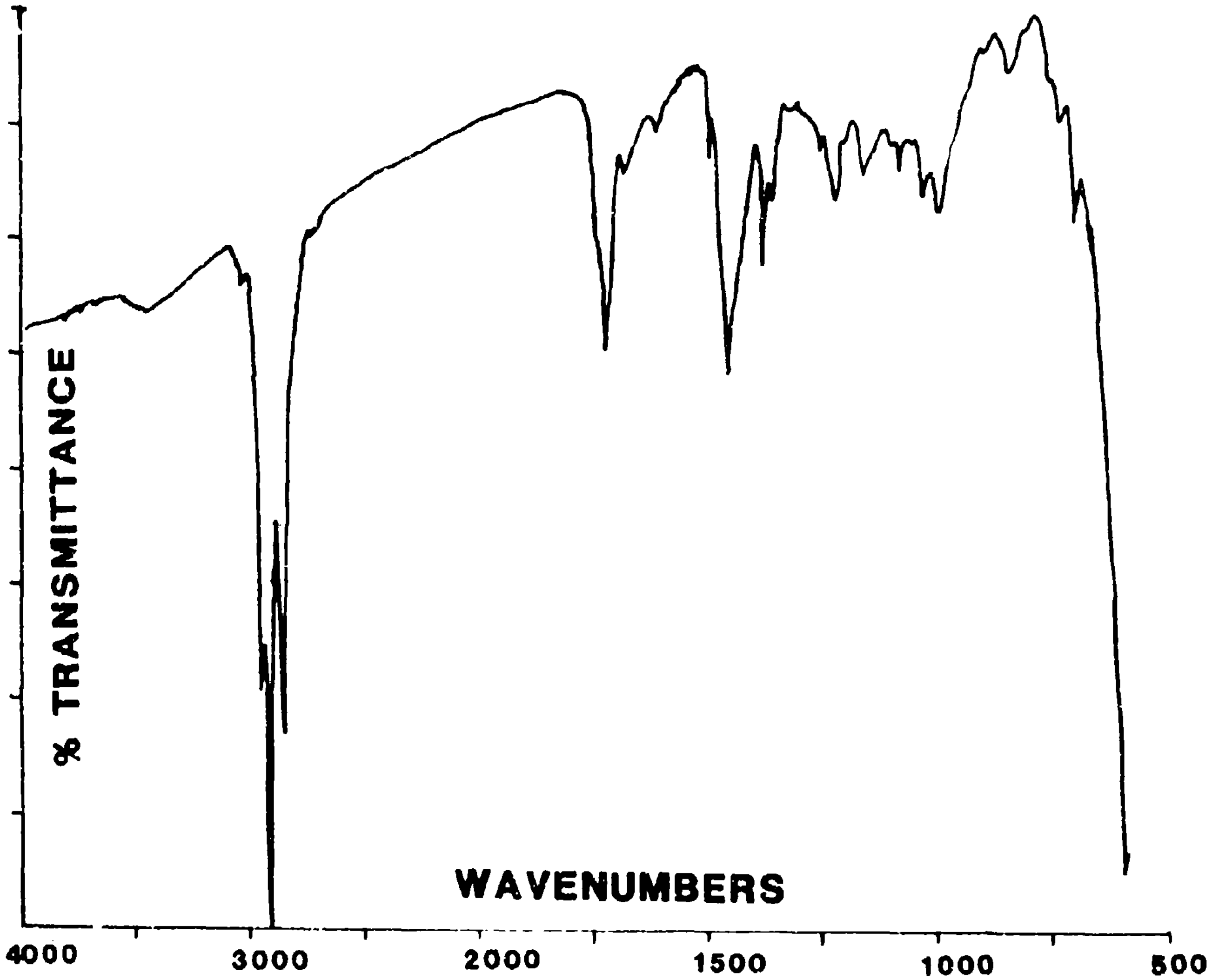


FIGURE 3, CARBON EXTRACT

2.4 Analysis Techniques

A Nicolet FTIR, Model MX-1 was used to analyze extracts from the propellant sections. As the DOA and DOZ migration rates could not be determined by infrared spectroscopy because the extractable urethane component of the propellant interfered, a Beckman Gel Permeation Chromatograph (2-50Å columns) equipped with a refractive index detector was used to measure DOA and DOZ. Table 1 summarizes the infrared spectrometer analysis conditions. All analyses were conducted using a 0.10 mm path cell with KBr windows.

TABLE 1. INFRARED ANALYSIS CONDITIONS

Labile Specie	Analytical Peak (cm^{-1})	Solvent	Quant.Range(g/ml)
DOP	1287	CCl_4	$(1-120)X10^{-4}$
ZL-496	2236	CCl_4	$(2-80)X10^{-4}$
CN-15	2238	$C_2H_4Cl_2$	$(2-120)X10^{-4}$
TMETN	1275	CCl_4	$(1-120)X10^{-4}$
SYEP	1608	$CHCl_3$	$(2-240)X10^{-4}$
TEGDN	1279	CCl_4	$(2-110)X10^{-4}$
Catocene	824	$C_2H_4Cl_2$	$(1-45)X10^{-4}$

For the distribution coefficient studies the temperature was 60°C and Formulations 1 and 4 with DOP as the plasticizer were used for all distribution coefficient studies. This was done to simplify the analysis since DOP is easily detected in the infrared region. Thus the only parameters measured would be those due solely to differences in DOP concentration or carbon pretreatment.

Complete propellant analyses followed the analysis scheme illustrated in Figure 4. A single 0.1 -gm strip of propellant was subjected to the extraction technique described earlier using each solvent successively. In all cases the solvents were A.C.S. reagent grade except the c-pentanone which was freshly distilled. The individual components from the CH_2Cl_2 extract were

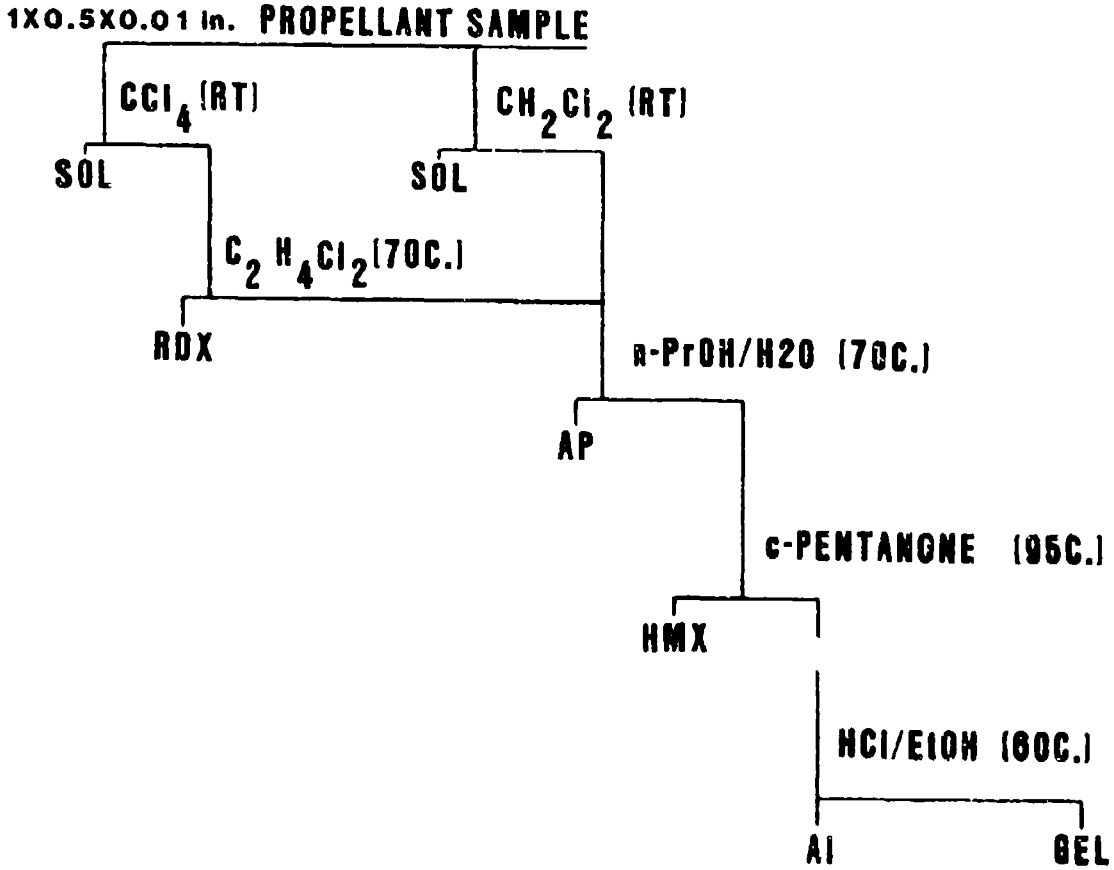


FIGURE 4, PROPELLANT ANALYSIS SCHEME

determined by FTIR spectroscopy and all others were determined by weight (aluminum was computed from the $AlCl_3 6H_2O$ resulting from its reaction with the HCl/EtOH). Normal propyl alcohol/water azeotrope (72%:28%) was selected because this mixture provided a high AP solubility and a constant boiling mixture which would not leave large amounts of water residue remaining on the upper porous strip. When aluminum was to be extracted, glass fiber mat was used instead of filter paper.

3. RESULTS AND DISCUSSION

3.1 Migration Rates

Figures 5 through 10 illustrate the migration rates of a number of labile ingredients. The ingredients were matched with the propellant formulations with which they would most likely be used. In Figure 5 there appears to be little difference in the rates of DOZ and DOA although they are at opposite ends of this molecular weight range. The migration rate of DOP is significantly slower possibly due to a lower solubility in the binder. Figure 6 shows the catocene migration rate through the same type of propellant. Catocene is very soluble in the binder and much more viscous than the plasticizers previously used. This may account for the significantly sharper change in concentration with depth and lower penetration. The relative rate of ZL-496 (a nonfunctional polybutadiene, MW ~ 3000) migration through the same propellant formulation is compared in Figure 7 to its rate through a liner formulation containing 33-percent carbon black. Although the liner contains 67-percent binder (HTPB/IPDI, 1:1.2) the rate of ZL-496 migration is significantly greater than in the propellant. In this case the migration rate must be controlled by the number of sites available in a cross section for material transfer. The relative migration rate of CN-15, a hydroxy terminated polymer consisting of copolymerized butadine and acrylonitrile (15%), is illustrated in Figure 8. The average molecular weight of this polymer is approximately the same as ZL-496; however, the viscosity is considerably higher. This difference in addition to possibly a lower solubility in the HTPB/IPDI binder likely accounts for the much lower migration rate. Figures 9 and 10 show the relative migration rates of trimethylolethyl methane trinitrate (TMETN), 1,3-bis (fluorodinitroethoxy)-2,2-bis

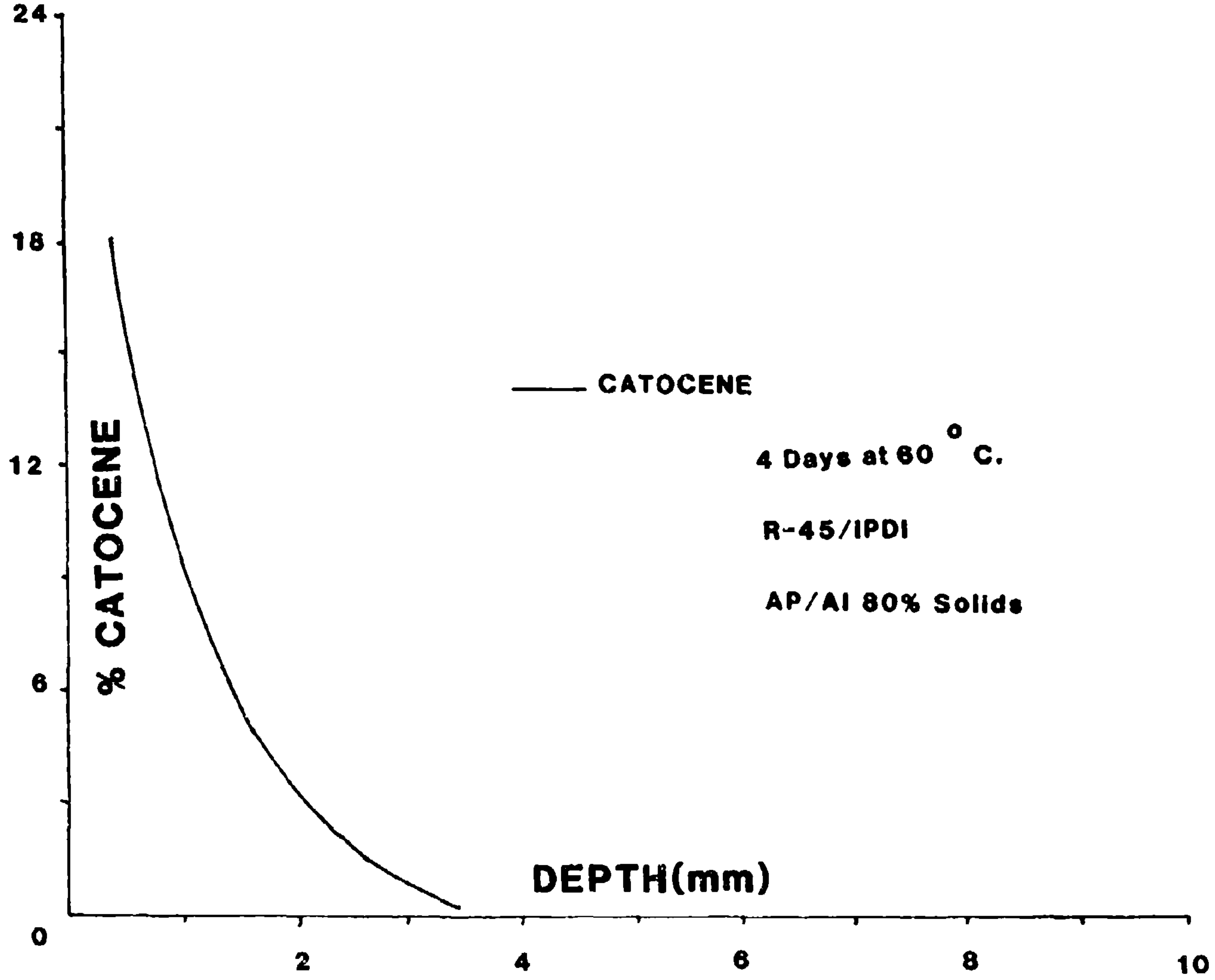


FIGURE 6, MIGRATION RATE

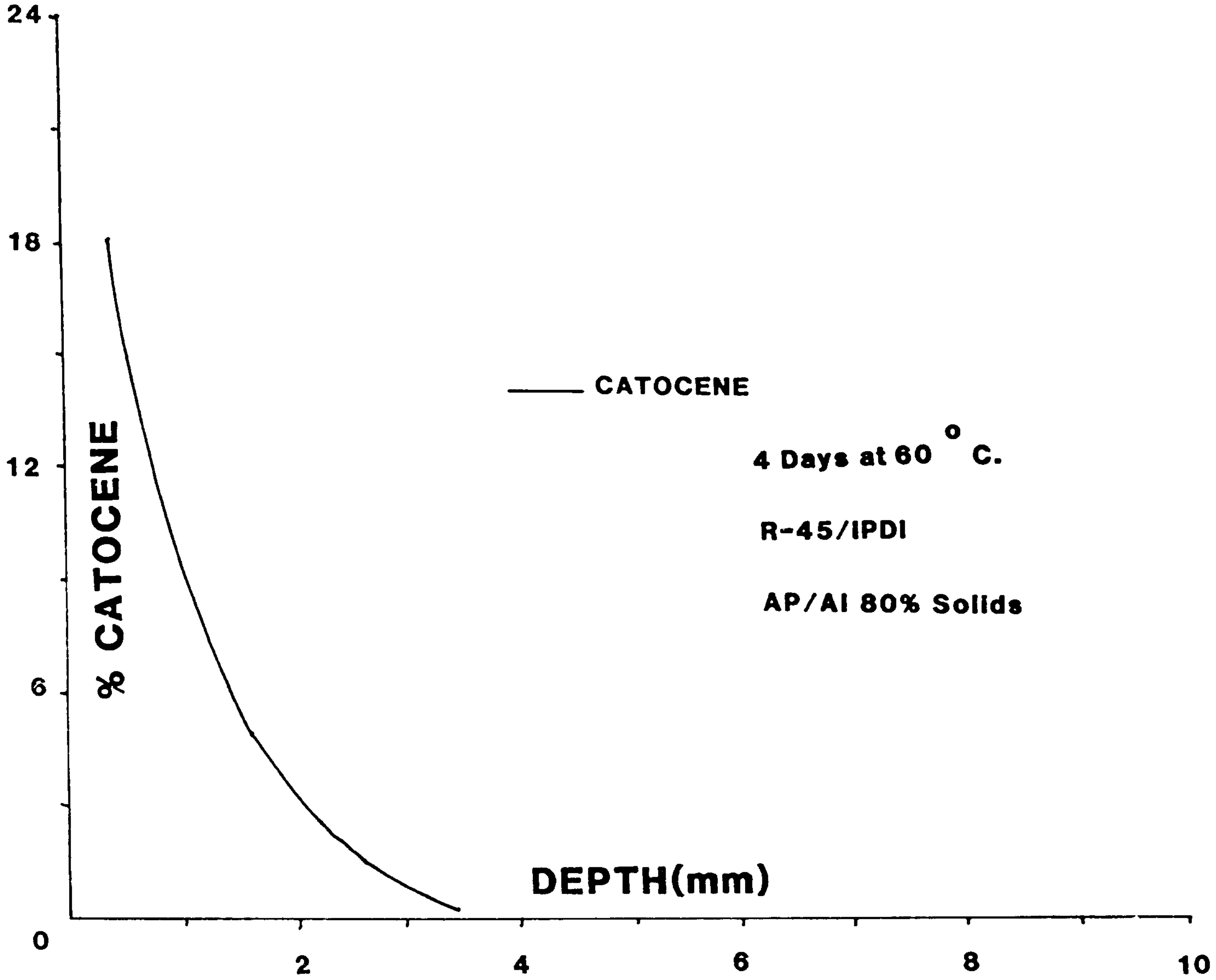
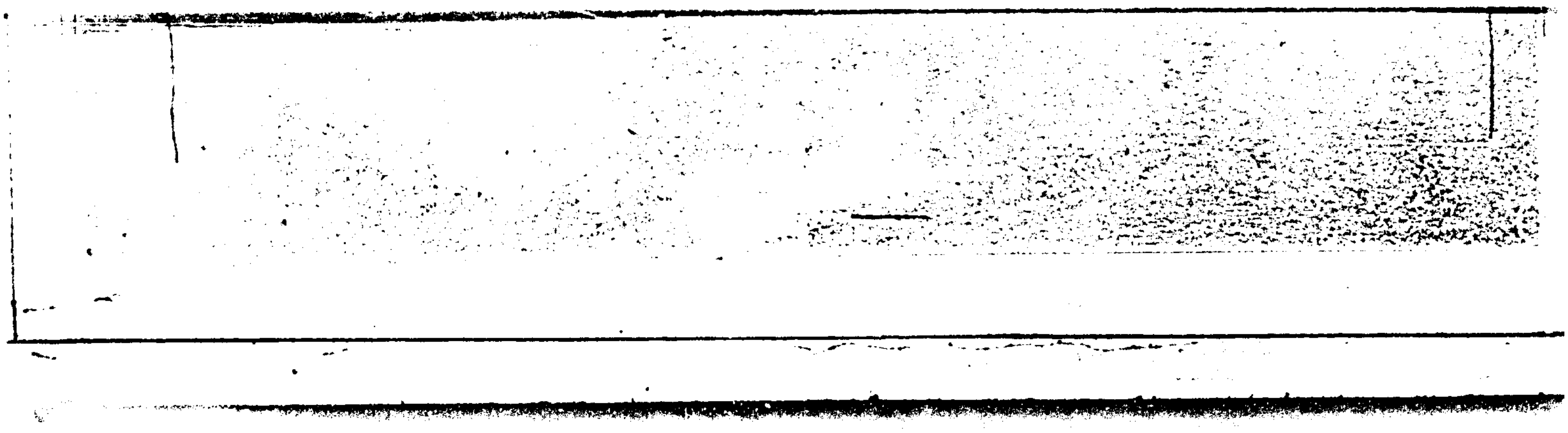


FIGURE 6, MIGRATION RATE



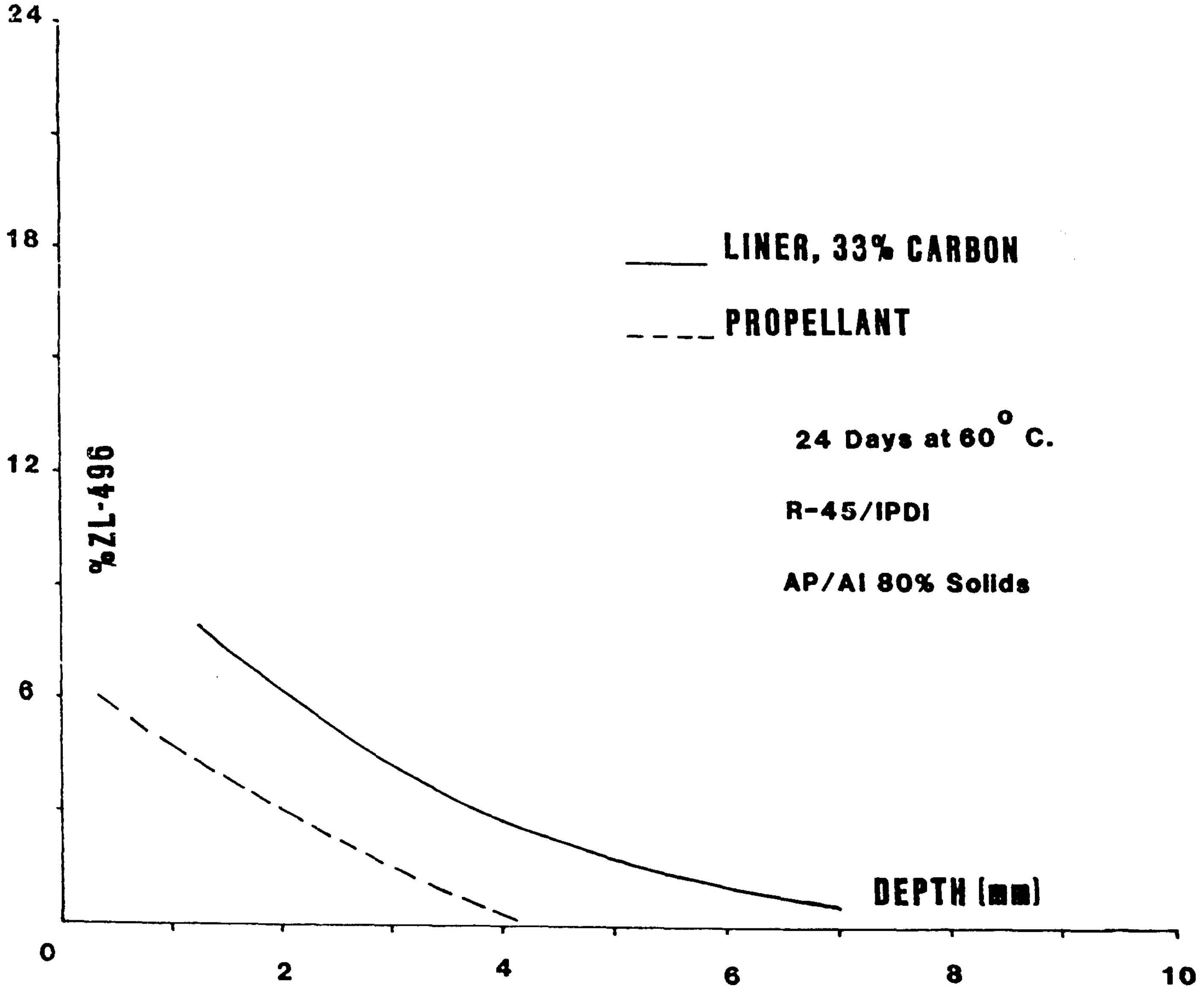


FIGURE 7, MIGRATION RATE

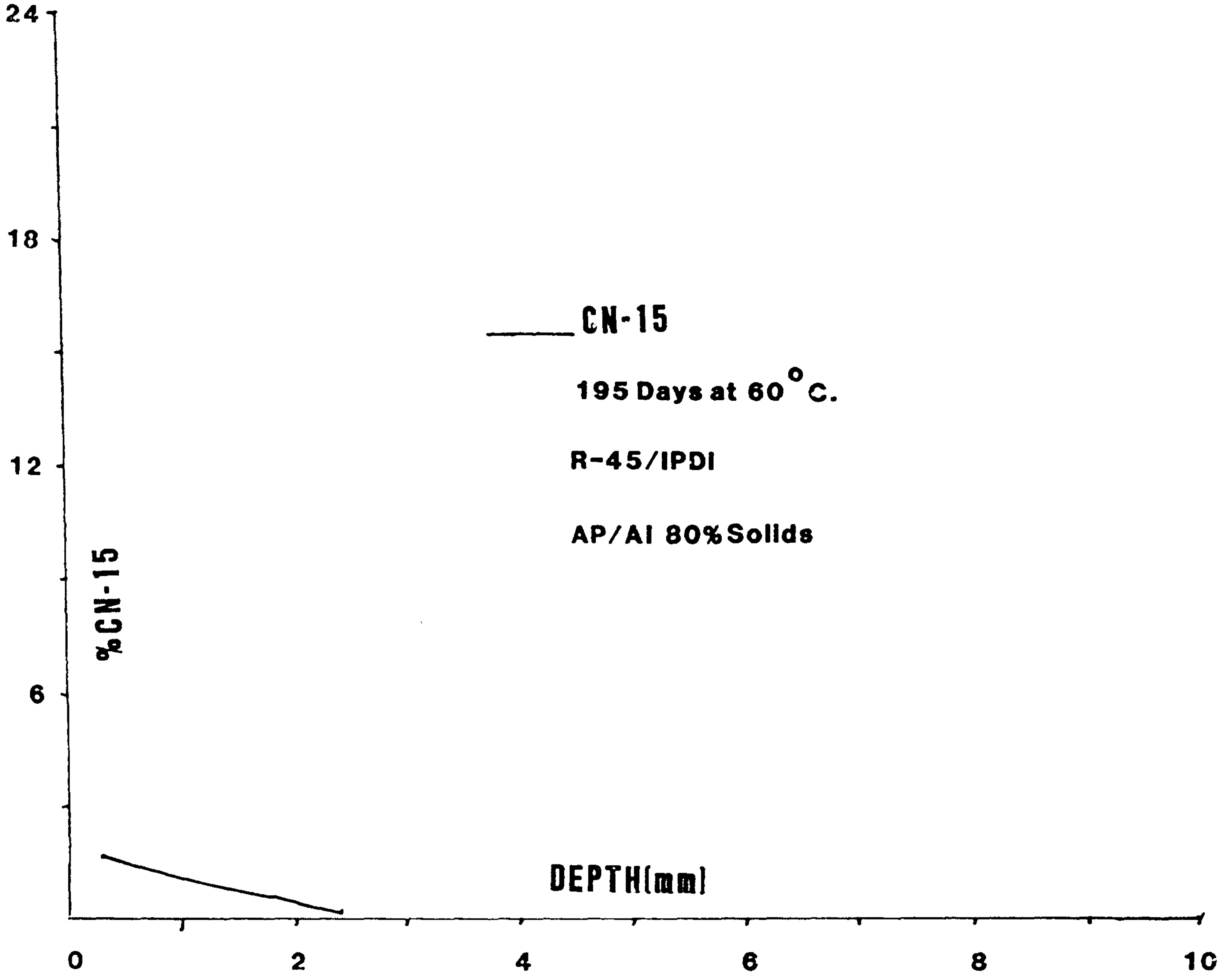


FIGURE 8, MIGRATION RATE

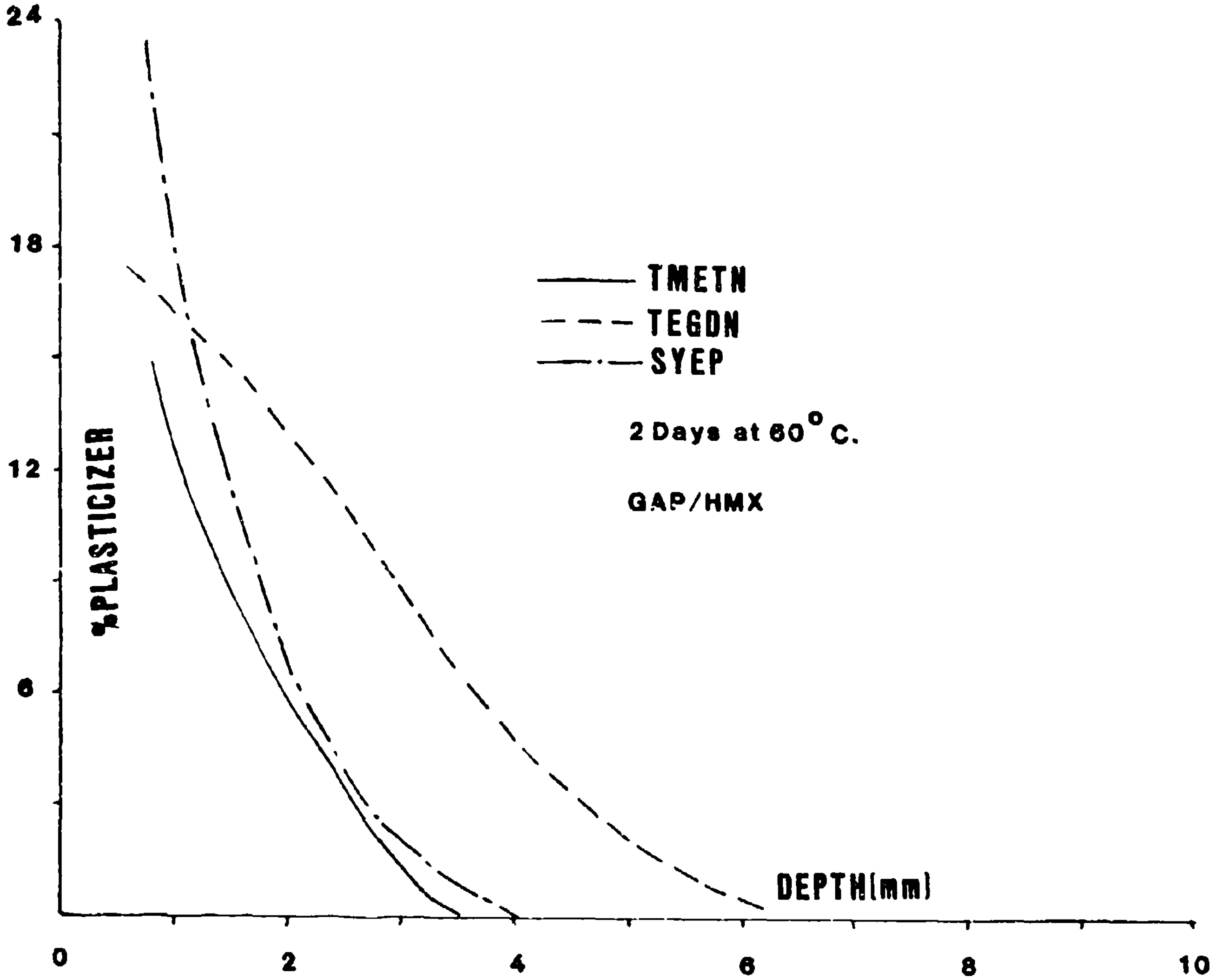


FIGURE 9, MIGRATION RATE

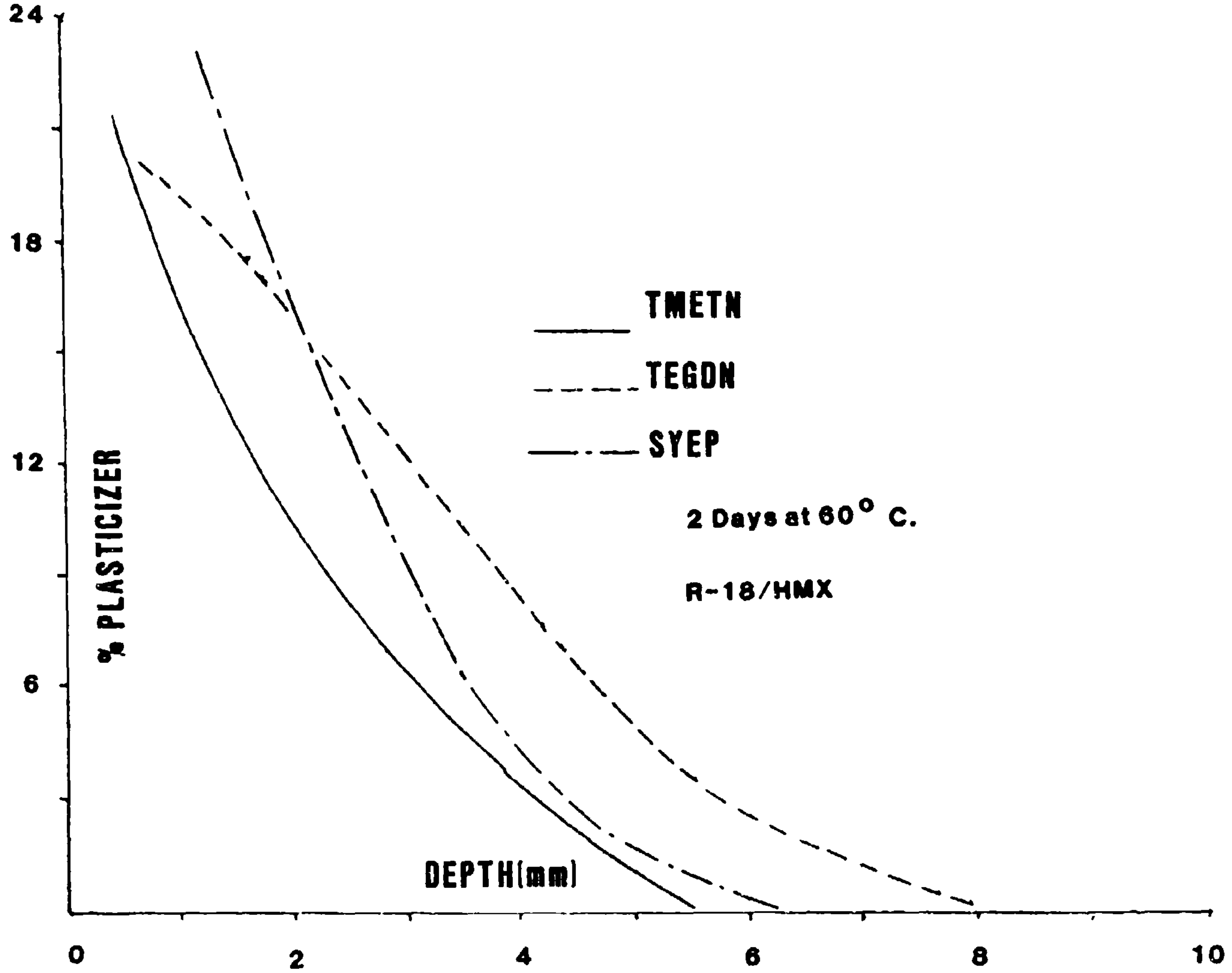


FIGURE 10, MIGRATION RATE

(difluoroamino) propane (SYEP), and triethyleneglycol dinitrate (TEGDN) through two minimum smoke formulations containing HMX and either GAP (glycidyl azide polymer) or R-18 (a polyester) as the binder. Again the rates do not appear to be related to molecular weight but are possibly related to the viscosity and solubility (ability to swell the crosslinked polymer) of the material in the binder. Thus far, no specific characteristics of the plasticizers or binders which allow easy prediction of the relative migration rates are apparent.

3.2 Distribution Coefficient

All distribution studies were made with propellants containing 60-percent ammonium perchlorate (50μ), 20-percent aluminum (27μ), and 20-percent total binder (HTPB/IPDI, 1:1) plus DOP at known starting concentrations. All liners used contained 30-percent carbon and 70-percent total binder (HTPB/IPDI, 1:1.2) plus DOP balanced for a particular propellant formulation. In all of the following data "balanced" means that the DOP concentration in the binder fraction of liner equaled the DOP concentration in the binder portion of the propellant. "Unbalanced" means that the propellant is mismatched with the liner (i.e., 3% DOP propellant with liner balanced for 1.5% DOP propellant and *vice versa*). Table 2 shows the DOP distribution between balanced precured liners and precured propellants attached with a film of uncured balanced liner. Each combination was aged at $60^{\circ}C$ for 60 days.

TABLE 2. DOP DISTRIBUTION, PRECURED PROPELLANT

%DOP			%DOP		
Liner		Propellant	Liner		Propellant
7.65	init.	3.05	4.02	init.	1.52
7.63	found	3.02	3.88	found	1.48

$^{*}C_D$ = 2.51 init., 3.53 found

$$^{*}C_D = \frac{\%\text{DOP Liner}}{\%\text{DOP Propellant}}$$

No DOP migration was indicated with precured propellants and balanced liners after 60 days of aging.

All of the following tests were conducted similarly except that only the liner was precured; the propellant and liner tack coat were cured and aged for a total of 60 days at 60°C in contact with the precured liner. Table 3 illustrates the data for both balanced and unbalanced combinations.

TABLE 3. DOP DISTRIBUTION WITH NORMAL CARBON PRETREATMENT

Balanced Liner	Unbalanced Liner
2.2% DOP Propellant	2.2% DOP Propellant
C_D init. 3.5	C_D init. 1.7
C_D found 4.0	C_D found 3.9
1.1% DOP Propellant	1.1% DOP Propellant
C_D init. 3.5	C_D init. 7.0
C_D found 3.9	C_D found 3.9

The Table 3 data indicates that the formulator has almost no control over the plasticizer content of the liner regardless of attempts to balance the system. The equilibrium C_D at least at 60°C appears to be 3.9 instead of the predicted 3.5 and DOP migrates in either direction through the interface to achieve that distribution.

A third distribution experiment was conducted wherein the carbon black used in the liner formulation was either predried at 160°C and 0.01 mm Hg for 72 hours or exposed to 90-percent relative humidity for 21 days. In all other respects the formulations and test conditions were the same as the previous experiment with theoretically balanced liners. Table 4 describes the results with wet and dry carbon liner formulations.

TABLE 4. DOP DISTRIBUTION, BALANCED LINER, WET AND DRY CARBON

Liner (dry carbon)	Liner (dry carbon)
1.0% DOP propellant	2.08% DOP propellant
C_D init. 3.5	C_D init. 3.5
C_D found 3.96	C_D found 4.26
Liner (wet carbon)	Liner (wet carbon)
1.0% DOP propellant	2.08% DOP propellant
C_D init. 3.5	C_D init. 3.5
C_D found 3.88	C_D found 4.01

Adsorption of DOP resulting from increased activation of the carbon black was not noticeable except possibly in the case of the 2.08-percent DOP propellant/dry carbon combination. Although no quantitative measurements were performed, the propellant formulations exposed to the dried-carbon-containing liners were noticeably softer and the adhesion of the liner to the propellant was significantly poorer than were the propellants exposed to wet carbon containing liners. Apparently the IPDI from the uncured propellant is adsorbed by the dried carbon, but the water from the wet carbon reacts with the excess IPDI in the cured liner or the water is not transferred to the propellant through the interface.

Because the results of the previous distribution coefficient studies were somewhat surprising, these tests were repeated using the same propellant and liner formulations but slightly different DOP levels. All of the liners were precured and the test fixtures were assembled with cured liner matching liner tack coat and the uncured propellant. Table 5 shows the distribution of DOP using both balanced and unbalanced liners. The carbon pretreatment in this case was "Normal".

TABLE 5. DOP DISTRIBUTION WITH NORMAL CARBON PRETREATMENT

Balanced Liner	Unbalanced Liner
3% DOP Propellant	3% DOP Propellant
C_D init. 3.50	C_D init. 1.74
C_D found 4.1	C_D found 3.5
1.5% DOP Propellant	1.5% DOP Propellant
C_D init. 3.51	C_D init. 7.05
C_D found 3.9	C_D found 3.7

The results are similar to the Table 3 data. The worst bond (very tacky propellant) occurred with the initial C_D of 7.05. Obviously a considerable quantity of DOP had to migrate into the propellant from the liner to lower the C_D to 3.70. In all of the samples (including those following) the DOP concentration in the propellant was uniform indicating that equilibrium was likely achieved after the 2-month storage at 60°C. The DOP distribution data for similar propellant/liner mixtures is presented in Table 6. The only difference in Table 6 is that the carbon used in the liner was "Dried".

Table 6. DOP DISTRIBUTION WITH DRIED CARBON PRETREATMENT

Balanced Liner	Unbalanced Liner
3% DOP Propellant	3% DOP Propellant
C_D init. 3.50	C_D init. 1.84
C_D found 4.00	C_D found 3.70
1.5% DOP Propellant	1.5% DOP Propellant
C_D init. 3.67	C_D init. 7.01
C_D found 3.80	C_D found 3.90

Generally all of the bond lines were stronger than with the "Normal" carbon treatment. However, in this case, both of the 1.5-percent DOP propellant combinations yielded the best bondlines and propellant characteristics (no soft propellant). Further DOP distribution data using "Wet" carbon pretreatment liner is shown in Table 7.

TABLE 7. DOP DISTRIBUTION WITH WET CARBON PRETREATMENT

Balanced Liner	Unbalanced Liner
3% DOP Propellant	3% DOP Propellant
C_D init. 3.51	C_D init. 1.75
C_D found 3.90	C_D found 4.00
1.5% DOP Propellant	1.5% Propellant
C_D init. 3.50	C_D init. 7.01
C_D found 3.70	C_D found 3.70

As with the "Dried" carbon liners, all of the bondlines were relatively strong but the unbalanced 3-percent DOP propellant/liner combination indicated the best bond. Table 8 shows DOP distribution data with a propellant/liner combination in which the carbon was first exhaustively extracted with CH_2Cl_2 and then dried as in the "Dried" carbon pretreatment.

TABLE 8. DOP DISTRIBUTION WITH EXTRACTED/DRIED CARBON PRETREATMENT

Balanced Liner	Unbalanced Liner
3% DOP Propellant	3% DOD Propellant
C_D init. 3.51	C_D init. 1.75
C_D found 3.8	C_D found 3.5
1.5% DOP Propellant	1.5% DOP Propellant
C_D init. 3.50	C_D init. 7.01
C_D found 3.9	C_D found 4.0

In this case the best bondline was found with the balanced 3-percent DOP propellant. The liner characteristics were significantly improved. All were more uniform in appearance and totally free from voids whereas with other carbon pretreatment methods some voids were always present. The worst propellant charcteristics were found with the unbalanced 3-percent propellant.

3.3 Migration Depth

To assess the propellant depth that is affected by these relatively short term distribution studies, several test fixtures were assembled in which the propellant thickness was 1-inch instead of the normal ¼-inch depth. This data from two months storage at 60°C is shown in Figures 11 and 12. It is obvious that the propellant within 1 centimeter (0.39 in.) of the interface is significantly affected by plasticizer migration even after this relatively short storage time.

3.4 Complete Propellant Analysis

Table 9 shows the results of several cured propellant analyses.

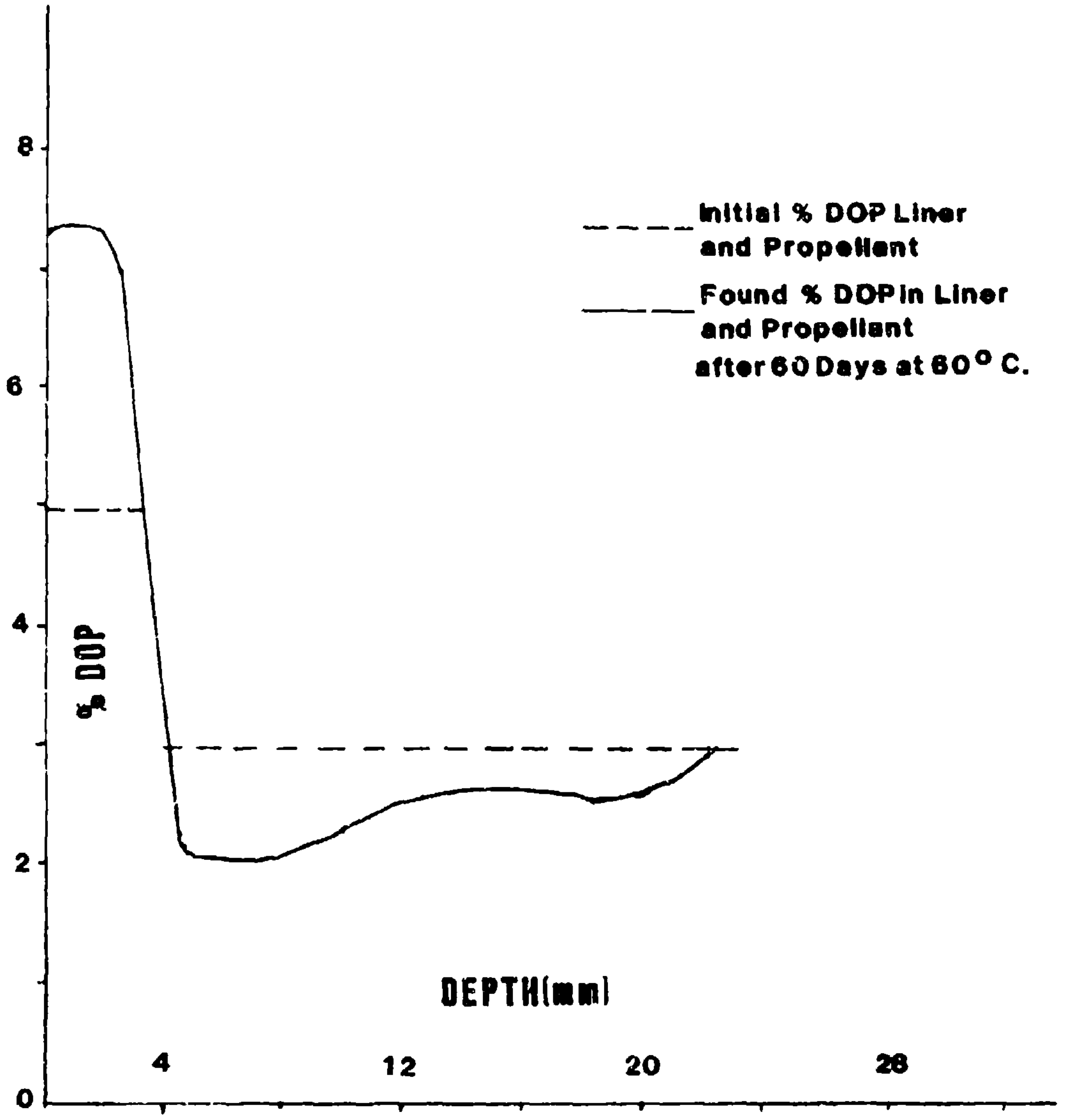


FIGURE 11, 3% DOP,UNBALANCED LINER

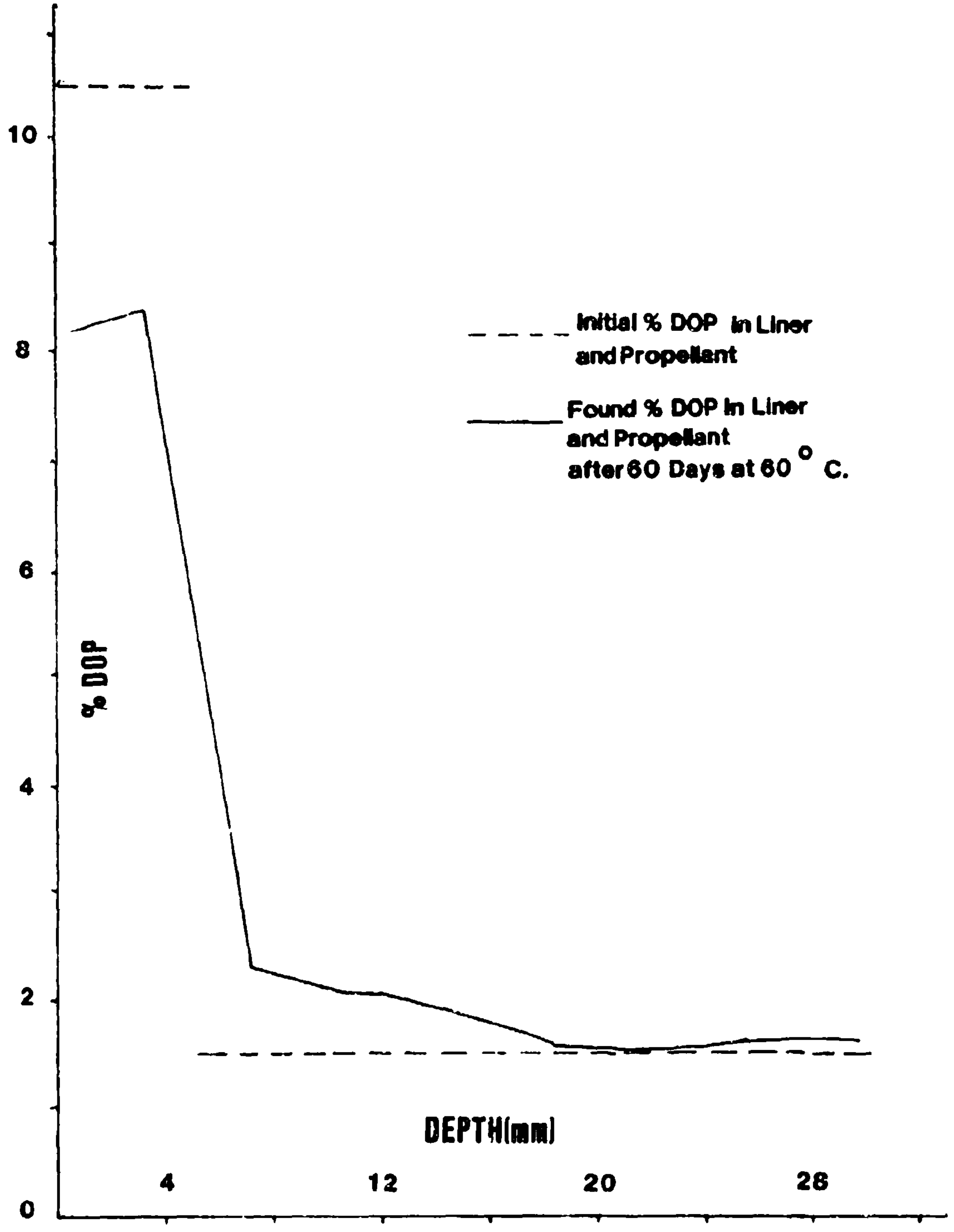


FIGURE 12,1.5 % DOP,UNBALANCED LINER

TABLE 9. PROPELLANT ANALYSIS RESULTS

	Propellant A	B	C	D
%4NDPA	N/A	0.54/0.6	----	----
%TMETN	N/A	14.4/15.7	10.5/10.8	----
%AP	68.5/69*	14.2/14	37.4/37	56.9/57
%HMX	N/A	44.9/45	23.9/25	12.1/12**
%AL	18.5/19	18.8/19	N/A	----
%Sol	6.03/7.06	----	----	----
%Gel	9.61/5.19	----	----	----

*Found/Theo.
**RDX

N/A = Ingredient not present

---- = Present but not quantized

Replicate data scatter was normally ±0.2 percent or less, except in the case of HMX. HMX crystallized in the gamma form and did not strongly adhere to the tab; thus some material loss may occur due to sample handling necessitating great care be exercised. Low TMETN results for Propellant B were attributed to thermal losses because this sample had been aged for a number of months at 57°C. The TMETN results for Propellant C, which had only an ambient thermal history, are much closer to the theoretical composition. The sol/gel results for Propellant A are significantly different from those shown for the conventional sol/gel analysis method. Sources of error such as scaling, incomplete solvent removal, and loss of AP to the sol fraction with the conventional method may account for these differences. Often it was difficult to remove the remaining gel from the extraction device to get a direct measurement. We are currently developing procedures for overcoming these problems. Although Propellant D contained other ingredients, the table includes only the date shown to demonstrate the recovery of RDX.

Table 10 shows the analysis results from a dissected SRAM motor. ZL-496 was used as the plasticizer and was not originally formulated with the insulation; however, the data indicates substantial migration of this material occurred.

TABLE 10. SRAM PROPELLANT ANALYSIS RESULTS

	%ZL-496	% Burnrate Catalyst	%AP
Insulation			
bonded*	2.0	7.7	N/A
released	2.4	7.6	N/A
Liner			
bonded	6.0	11.2	N/A
released	9.0	11.7	N/A
Propellant (< 0.2 in.)			
bonded	1.9	0.7	70.4
released	2.9	1.4	71.4
Propellant (> 0.2 in.)			
bonded	3.8	1.7	---
released	4.2	1.7	---

*bonded/released refers to regions in the motor where the insulation was or was not purposely bonded to the motor case.

The most significant composition variations appear to have occurred within 0.2 in. of the propellant/liner interface. In all cases, the only source of ZL-496, now present in the insulation, was the liner and adjacent propellant.

4. CONCLUSIONS

4.1 Migration Rate

No general rule for predicting migration rate could be determined from the data. The migration rate of a labile ingredient through precured propellant appears to be directly proportional to its solubility in the binder and inversely proportional to its viscosity and the solids content of the binder. Migration of solid ingredients is also possible if they are somewhat soluble in one of the liquid ingredients. Another area of migration phenomena which was not studied quantitatively is the influence of a rapidly migrating specie on the migration rate of a slowly migrating ingredient. Molecular weight does not appear to be a major factor but molecular structure (i.e., branched molecules versus linear) may be. If it is assumed that a infinite supply of pure plasticizer is located on one surface of the propellant formulation, then the depth (D) of migration after time (t) can be expressed as follows:

$$D = \sum_{0}^{i} (Ri)t$$ where: Ri is the migration rate at a depth increment

The rate of migration is controlled by numerous factors including binder concentration, solubility, viscosity, plasticizer concentration, and other interactions (i.e., carbon activity). These factors can be empirically related as follows:

$$Ri = f(bi) + f(ci) + f(s)\,T + f(ri)\,T + f(1/v)\,T$$

Where: bi = binder concentration at depth i

ci = plasticizer concentration at depth i

s = plasticizer solubility in the binder

ri = plasticizer interaction with components other than binder at depth i

v = plasticizer viscosity

It is obvious that an expression of migration rate is extremely complex and the relative importance of each factor will be difficult to predict without further study.

4.2 Distribution Coeffficient

The principle conclusion that can be drawn from this data is that the conventional methodology for balancing propellant/liner combinations is erroneous at least for DOP. In fact, it appears that the formulator has little influence on the distribution coefficient of a labile ingredient. In the cases where both the liner and the propellant were precured prior to contact, no change in the distribution coefficient was observed. This does not imply that thermodynamic equilibrium exists. The data simply illustrate that at these low plasticizer concentrations the DOP migration rate is too slow to yield an observable change in the distribution coefficient within the 2-month aging period. In contrast the migration rates in uncured propellants were sufficiently rapid to yield observable distribution coefficient changes after two months. The bond strength near the interface on the propellant side (0.5 mm from the liner) was generally weaker than the actual interface. This was true regardless of whether C_D increased or decreased. Except the marked improvement in the quality of the dried extracted carbon liner, no positive differences could be related to the various carbon pretreatment methods. Apparently some curative either consistently migrated into the liner regardless of the direction of DOP flow or it was partially washed from the interface region by the DOP and was carried either into the liner or deeper into the propellant. In actual propellant formulations a soft region near the interface is occasionally encountered. However, adjacent to the soft region, an overcured or hard zone is also found either next to the propellant/liner interface or deeper in the propellant. This phenomenon could be explained by the relocation of curative resulting from plasticizer migration. In contrast to the formulations used in this study, most actual propellant formulations are undercured which would lead to hard propellant regions when too much curative is located in a particular zone. This type of distribution study does appear to be necessary in the development of any new solid propellant formulation.

4.3 Complete Analysis

The preceeding ingredient separation scheme allows the analyst to completely characterize the chemical composition of as little as 100 milligrams of solid propellant. Thus there should be innumerable applications for this separation scheme and/or the device described herein. Further studies concerning microscale cured propellant characterisation such as oxidizer particle size distribution are currently in progress.

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GLOSSARY

AP - Ammonium Perchlorate

ATR - Attenuated Total Reflectance

CN-15 - Hydroxy terminated polybutadiene copolymerized with 15% acrylonitrile

DOA - Dioctyl Adipate

DOP - Di-n-octyl Phthalate

DOZ - Dioctyl Azelate

FTIR - Fourier Transform Infrared

GAP - Glycidyl Azid Polymer

HDI - Hexanediisocyanate

HMX - Octahydro-1,3,5,7-tetranitro-S-tetrazene

HTPB - Hydroxy terminated polybutadiene

IPDI - Isopherone Diisocyanate

RDX - Hexahydro-1,3,5-trinitro-S-triazine

R-18 - Hydroxy terminated polydiethylene glycol Adipate

SYEP - 1,3-Bis (Fluorodinitroethoxy)-2,2-bis(difluoro amino) Propane

TEGDN - Triethylene glycol Dinitrate

TMETN - Trimethylol-ethyl Methane Trinitrate

ZL-496 - A Nonfunctional Polybutadiene (MW $\sim$ 3000)

Corrected page

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SOLID PROPELLANT INGREDIENT MIGRATION STUDIES

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NOTICE

This is a report of a research and development study that was conducted under in-house AFRPL Project Number 573005RE, Task III. This report covers the work conducted at the Air Force Rocket Propulsion Laboratory, Edwards AFB, California during the January 1980 to December 1982 time period. The principal investigator of this project was Louis A. Dee. Portions of this report have been presented by the authors at the JANNAF Propulsion Meeting, New Orleans, Louisiana (May 1981) and at the JANNAF Propellant Characterization Meeting, A.F. Academy, Colorado Springs, Colorado (August 1981).

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