DEVELOPMENT OF PEX EXPLOSIVES
PHASE DIAGRAM STUDIES

B. D. Faubion

DEVELOPMENT DIVISION

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DEVELOPMENT OF PEX EXPLOSIVES

PHASE DIAGRAM STUDIES

ABSTRACT

Experiments have been carried out to determine the solid-liquid phase diagrams of binary mixtures of FEFO, EDNP, BDNPA and BDNPF. Cooling curves for the mixtures give no indication of crystal formation.

Penetration measurements indicate a glass transition for all of the mixtures below -40 C. The existence of glassy states for the mixtures was confirmed by visual observation with a polarizing microscope.

Thermomicroscopy has been used in the preliminary study of the phase behavior of four binary mixtures. So far no eutectic has been observed.

INTRODUCTION

In order to achieve a successful PEX explosive formulation based on dispersions of HMX in energetic liquid vehicles, the vehicles must remain fluid over a temperature range from -65 to 165 F. At the present time no pure substance has been found with the desired characteristics. It was therefore necessary to investigate the solid-liquid phase diagrams of various energetic mixes in search of a eutectic composition which is fluid at -65 F. Several materials have been proposed for study(1). Mixtures of four materials have been investigated so far in this study: Bis-(2,2-dinitro-2-fluoroethyl) formal (FEFO); Ethyl 4,4-dinitropentanoate (EDNP); Bis-(2,2-dinitropropyl) formal (BDNPF) and Bis-(2,2-dinitropropyl) acetal (BDNPA).

EXPERIMENTAL METHODS

Several experimental techniques can be used in the investigation of a phase diagram. A brief review of the various techniques is given by Haase and Schonert(2). Thermal analysis, i.e., the use of cooling or heating curves, is the most common method. The temperature of the sample is measured as a function of time during heating or cooling. A change in the heating rate is observed during the disappearance or appearance of a phase due to the accompanying enthalpy change. To use this method to investigate the phase diagram of two components, it is necessary to obtain cooling curves for several mixtures. This method is not only time consuming, but is particularly affected by a problem common to any method, i.e., incompletely or slowly established equilibrium. The most usual non-equilibrium state in solid-liquid equilibria is that of supercooled liquids which change to glasses. The materials used in this investigation are particularly bad in this respect.

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DEPARTMENT OF JUSTICE

WASHINGTON, D. C.

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[Illegible Address]

Enclosed for the Attorney General are two copies of a letterhead memorandum dated and captioned as above.

Very respectfully,
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Very truly yours,
[Illegible Signature]

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Dilatometric methods may also be used to study solid-liquid phase diagrams. The usual procedure is to measure the volume of the sample as a function of temperature. A variation of this method was used in this study. The temperature at which a 0.025-inch probe penetrated the frozen sample during heating was determined using the thermal mechanical analyzer (TMA) attachment on the DuPont DTA. Although this method is extremely sensitive, it is still plagued by the same problems as the cooling curve method.

A third method used extensively in the study of solid-liquid phase diagrams is thermomicroscopy. This technique is described in detail by McCrone(3). To determine the solid-liquid phase diagram of a binary mixture, a mixed fusion is prepared. A mixed fusion for microscopic examination is prepared by first melting the higher melting component under a cover glass on the microscope slide and allowing it to resolidify. The solid should ideally occupy only half the area under the cover glass. The low-melting component is then placed at the edge of the cover glass and heated so that it melts and runs under the cover glass into contact with the first component. Careful observation of the zone of mixing during the crystallization process indicates the existence of a eutectic, addition compound, solid solutions, and unstable polymorphs. The slide is then placed on a hot stage and the zone of mixing observed as the temperature is raised. The melting points of all solid phases present can usually be measured during a single heating. Under ideal conditions, the essential characteristics of a binary eutectic diagram can be determined in two to four hours. When a polarizing microscope is used, it is also easy to distinguish between a glassy and crystalline solid. This method was chosen as the best method for investigating the phase diagrams of the energetic liquid vehicle mixtures.

In order to apply this method in this investigation it was necessary to have a microscope hot stage capable of operating over the temperature range from -65 to 165 F. Although no commercially available hot stage met this requirement, the Leitz cold stage (-20 to 350 C) was adapted for use at temperatures down to -120 C. This was accomplished by cooling the stage with dry nitrogen instead of carbon dioxide gas. The nitrogen was passed through a coil of copper tubing immersed in a 2-liter dewar of liquid nitrogen. To prevent frost from condensing on the sample and microscope objective, the cold stage and microscope were both placed in a Plexiglas box which was purged with dry nitrogen. A rubber glove in one side of the box allowed manipulation of the sample. The microscope tube protruded through a hole in the top of the box and was equipped with a Zeiss C35M automatic camera and adaptor with viewing telescope. A Unitron MPS polarizing microscope was used with a 10X objective and ocular. The temperature of the cell was measured using a Chromel-Alumel thermocouple, the output of which was plotted as a function of time on an X-Y Recorder (Mosley 2D-2). Photographs were taken during cooling and heating of the samples using High-speed Ektachrome Type B film (EHB-135) which was developed to an ASA speed of 320.

RESULTS AND DISCUSSION

THERMAL ANALYSIS

Attempts to measure the freezing points of FEFO, BDNPA, BDNPF, and EDNP were unsuccessful. None of the curves showed a discontinuity in the cooling rate. It appears that in all cases the liquids supercooled and changed to glasses. No attempts were made to induce crystallization other than cooling the sample.

PENETRATION ANALYSIS

The DuPont thermomechanical analyzer was then used to measure the temperature at which a 0.025-inch probe penetrated the sample. Penetration measurements were made on the pure materials and on various binary mixtures. In each case one-gram samples of the mixtures were prepared by thoroughly mixing the carefully weighed components. A sample (~ 100 mg) of each mixture was weighed in an aluminum DSC sample cup and quenched on a block of dry ice. The sample was then placed in the apparatus and immersed in a dewar of liquid nitrogen. The temperature was then raised to above the transition point. Fig. 1 shows a typical penetration curve. The penetration temperatures are shown in Tables I - III. Measurements were not made on mixtures of EDNP with the other materials due to the lack of a pure sample at the time these measurements were being made.

All of the penetration temperatures are unrealistically low indicating that the samples did not crystallize, but again formed glasses.

THERMOMICROSCOPY

Thermomicroscopy proved to be the most successful method for studying the solid-liquid phase diagrams of the chosen materials. Still, certain problems were encountered which make it difficult to describe the phase behavior with certainty. The main problem, as previously encountered, is the ability of these materials to supercool well below their freezing point and transform to a glassy solid. The existence of a glassy state at low temperatures for all of the materials has been confirmed by visual observation with polarized light. Considerable effort was required to induce crystallization of EDNP and FEFO. It was necessary to repeatedly thermal cycle the sample and scratch the surface of cover glass. This lengthened the time necessary to examine a sample to about one week. BDNPA and BDNPF could easily be crystallized by seeding the melt slightly below room temperature.

Another problem, pointed out by McCrone(3), is more serious as it can lead to an erroneous interpretation of the phase diagram. Under certain conditions the equilibrium phases may not nucleate and will not be observed. For example, the eutectic may not nucleate because of rapid supercooling and the system will completely crystallize without a fine-grained eutectic mixture. This makes it necessary to confirm the microscopic observations using other experimental techniques.

Fig. 1. Penetration Curve for 50/50 BDNPA/BDNPF Mixture

Table I. Penetration Temperatures for
FEFO/BDNPA Mixtures

<u>% FEFO</u>	<u>% BDNPA</u>	<u>T_p C</u>
100	0	-70
90	10	-65
80	20	-58
70	30	-61
60	40	-57
50	50	-54
40	60	-54
30	70	-50
20	80	-48
10	90	-46
0	100	-45

Table II. Penetration Temperatures for
FEFO/BDNPF Mixtures

<u>% FEFO</u>	<u>% BDNPF</u>	<u>Tp C</u>
100	0	-70
90	10	-65
80	20	-63
70	30	-59
60	40	-58
50	50	-55
40	60	-54
30	70	-51
20	80	-50
10	90	-48
0	100	-47

Table III. Penetration Temperatures for
BDNPA/BDNPF Mixtures

<u>% BDNPA</u>	<u>% BDNPF</u>	<u>Tp C</u>
100	0	-45
90	10	-45
80	20	-46
70	30	-46
60	40	-45
50	50	-46
40	60	-46
30	70	-45
20	80	-46
10	90	-45
0	100	-47

Fig. 2. Color Print of FEFO Crystal

Fig. 3. Color Print of EDNP Crystals

Fig. 4. BDNPA Crystals at RT

Fig. 5. BDNPF Crystals at RT

Melting points of the four pure components have been measured and are in agreement with reported values(1). The melting points as determined microscopically are as follows:

FEFO	9 C
EDNP	- 7 C
BDNPF	32 C
BDNPA	30 C

Color photomicrographs were also made using polarized light of each solid to aid in identifying the components and distinguishing them from new phases. Figs. 2 - 5 show the crystal films observed when each solidifies between the cover glass and microscope slide. Fig. 2 also shows a well formed isolated crystal of FEFO which is growing from the melt.

Preliminary studies of the following binary systems have been completed:

FEFO/EDNP
EDNP/BDNPA
EDNP/BDNPF
BDNPA/BDNPF

So far no eutectic has been observed in any of these systems. This does not rule out the possibility that eutectic compositions may still exist for some of these mixtures. It is highly possible that the eutectics did not nucleate because of supercooling. In this case only the melting of the two components would be observed. The four binary systems studies all exhibit this behavior. If these systems do not in fact form eutectic mixtures, it will be necessary to determine the extent to which these components are soluble in the solid state. It would then be possible to assign these systems to one of the five Roozeboom type composition diagrams.

FUTURE WORK

The investigation of the phase diagrams of energetic liquid vehicle mixes is continuing. Additional binary and ternary mixtures of FEFO, EDNP, BDNPA and BDNPF will be examined by thermomicroscopy. When or if a eutectic is found, the composition will be determined (2,3 and 4).

Cooling curves and DTA thermograms will then be attempted on the eutectic mixture.

Other energetic liquids will also be examined to see if they form low melting eutectics with the four materials studies.

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