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HIGH EXPLOSIVE AND SOLID PROPELLANT COMPOSITIONS BASED UPON
A NEW CLASS OF SOLUBLE OXIDANTS (U)

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A NEW CLASS OF SOLUBLE OXIDANTS (U)

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HIGH EXPLOSIVE AND SOLID PROPELLANT COMPOSITIONS
BASED UPON A NEW CLASS OF SOLUBLE OXIDANTS (U)

I. ORGANIC OXIDANTS-PRELIMINARY REPORT

Prepared by:

O. H. Johnson

Approved by: Darrell V. Sickman
Chief, Organic Chemistry Division

ABSTRACT: A number of the oxygen-surplus experimental high explosive compounds discovered in the Bureau of Ordnance's research program in recent years, such as BTNEN, BTNEC and TNEOC, have been found to dissolve in high concentrations in several nitropolymers such as polynitropolyurethanes, polydinitropropyl acrylate and nitrocellulose. A preliminary study has been made of this phenomenon and it appears to be directly applicable to the formulation of a new class of high explosive or solid propellant compositions in which the oxidant is all or largely dissolved in the polymeric matrix. It has been found possible to prepare essentially homogeneous compositions with oxygen balances as high as the CO₂ level which can be extruded or compression molded into tough, cylindrical shapes. Some of the compositions can be machined to close tolerances. Most of them have good vacuum thermal stabilities at 100°C for 48 hours. Impact sensitivities were in the same range as double base propellants. The addition of aluminum powder did not materially affect either the thermal stability or impact sensitivity. Calculated heats of detonation of 1400-1600 calories/g are readily achieved by formulations containing no aluminum, while with the latter added, values to 2500 cal/g are attainable. This development will continue and this report is to be considered as preliminary study.

CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring, Maryland

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NAVORD Report 6677

10 July 1959

This report is the first of a series on the development of a new class of solid propellants and high explosives based upon the "soluble oxidant" concept. It utilizes as oxidants the group of surplus oxygen experimental explosive compounds, all but one of which were discovered in this laboratory as part of the Navy's research program on new high explosives. This work was originally undertaken under Task FR-44 in the hope of finding some new concept for the desensitization to a practical level of these very energetic but dangerously sensitive new high explosives. After the initial observation of their solubility in several nitropolymers, coupled with effective desensitization, the work was broadened to include solid propellant formulations as well. This forms the basis for future development work in explosives and propellants at the Naval Ordnance Laboratory.

MELL A. PETERSON
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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HIGH EXPLOSIVE AND SOLID PROPELLANT COMPOSITIONS
BASED UPON A NEW CLASS OF SOLUBLE OXIDANTS(U)

HISTORICAL

The Navy Bureau of Ordnance has since 1948 sponsored a chemical research program for new high explosives both in this laboratory and in a number of academic and industrial laboratories (1-4). This program has produced over 300 new explosive compounds the majority of which are derivatives of nitroform, $\text{HC}(\text{NO}_2)_3$. Compounds with oxygen contents never before attained in stable solid explosive compounds were successfully synthesized (14-18 incl.). In several cases the oxygen content per unit volume exceeded that of liquid oxygen itself. It was hoped that these compounds would be useful as explosive oxidants in high explosive compositions containing aluminum powder for use in underwater or air-blast warheads of the HBX-3 or H-6 types. Unfortunately, these high oxygen explosives (sometimes referred to as a class by the symbol "HOX") were found to be quite sensitive to impact (21). Furthermore, the usual desensitization techniques of wax coating or suspension in TNT failed to desensitize them sufficiently for military use until excessive amounts of the desensitization material had been used. Apparently, small amounts of such material merely acted as fuel for the excess oxygen in the compounds, producing a more energetic decomposition reaction in hot spot areas and thus promoting growth of these spots*.

It was thus apparent that a new approach was necessary. The classic work of Alfred Nobel on the effective desensitization of nitroglycerine by solution or "gelatinization" in nitrocellulose in 1888⁽⁶⁾ formed the basis for the present approach. Nitroglycerine is a liquid, however, and not a solid as are these high-oxygen explosives, but it is also far more sensitive to impact than are these HOX's.

If this technique was to be effective it was visualized that the HOX must be dispersed in molecular form between the chains of polymers or

*The same effect has been noted with organic coatings on ammonium perchlorate crystals in this and other laboratories⁽⁵⁾.

possibly in molecular aggregates sufficiently small to fit between these polymer chains, and with no tendency to crystallize further. This is what is meant by "solution" in the polymer. Such a situation is more difficult to attain with these solid, high density explosives where strong crystal lattice forces are possible than with a liquid such as nitroglycerine.

The Naval Ordnance Test Station is currently developing an energetic polymer from methyl-5-vinylnitrotetrazol for solid propellant applications. They reported to the author informally that a sample of TNEOC furnished by this laboratory appeared to dissolve in that polymer to the extent of about 75%. This was described at the Fourth JANAF Solid Propellant Group Meeting in May 1958⁽⁸⁾. That development with this particular polymer is continuing in that laboratory and is another example of this soluble-oxidant concept.

Further, the Allegany Ballistics Laboratory has been informed of these developments and furnished samples of several HOX's and is actively studying the use of BTNEN and TNEOC in nitrocellulose as a basis for higher energy solid propellants under Contract NOrd 16640.

OBJECTIVES OF FEASIBILITY STUDY

If this approach were to be successful, it was visualized that five major requirements must be met. These are as follows:

- (a) Formulations of very high energy content must be achieved in a practical way;
- (b) These formulations must be sufficiently insensitive for practical military safety handling;
- (c) They must possess sufficient storage and heat stability for minimum military requirements;
- (d) They must be capable of being formed into practical shapes for warhead or propellant grain applications;
- (e) They must possess certain minimum physical requirements of strength, density, elongation, etc., and as much homogeneity of fuel/oxidant as possible.

The feasibility of meeting these requirements was briefly studied experimentally and the results will be described below.

Energy Considerations

The high oxygen explosives, HOX's, and the nitropolymers considered for this investigation are tabulated together with their main physical properties in Appendices I and II. The symbols indicated for them will be used for convenience hereafter. Nitroglycerine is included for comparison purposes only. No polymers of commercial types without nitro oxygen were included, as simple calculations showed that to achieve the CO oxygen level in, for example, polyacrylonitrile, 81 weight percent of BTNEC would be required, which is beyond any possible solubility limit. The formulation considered most desirable energy-wise was a homogeneous matrix as rich as possible in oxygen, preferably to about the CO₂ level, to which aluminum powder could be added to reduce it to the optimum aluminum/oxygen ratio for airblast or underwater explosive or solid propellant applications. The homogeneity of organic fuel and oxidant should provide a fast reaction in the high explosives and a smooth fast burning together with better physical properties in the solid propellants, as well as the ability to regulate the oxygen-to-fuel ratio at will within the limits of the system. Calculated heats of detonation of several possible systems are shown in Table I. Calculated specific impulse of BTNEC as an HOX with two energetic fuels is shown in Table II.

SUMMARY OF RESULTS

It was soon found that from 50-70% of these HOX's could be incorporated by various techniques into these polymers without visual crystallization even under the microscope. A definite solubility limit was observed which was characteristic of each HOX in each polymer and above which crystallization occurred. These are shown in Table III and are rough values only. The presence of a third component such as a plasticizer altered these values, sometimes substantially.

In an effort to demonstrate true solubility, one system, namely, the BTNEC/PNU XIII-A system was studied by means of X-ray diffraction. This system was chosen as the polynitropolyurethane has practically no crystalline character and the diffraction pattern of crystalline BTNEC is readily identified in mixtures of the two.

TABLE I
CALCULATED HEATS OF DETONATION OF SELECTED
COMPOSITIONS(a)

Oxidant (%)	Fuel (%)	Aluminum	Products	Heat of Detonation cal/g
TNEOC (68)	NC (32) (b)	0	CO ₂ , H ₂ O	1425
BTNEN (62.7)	NC (37.3)	0	CO ₂ , H ₂ O	1625
BTNEC (84)	PNU XIII-A (16)	0	CO ₂ , H ₂ O	1395
TNEOC (83.2)	PNU XIII-A (16.8)	0	CO ₂ , H ₂ O	1515
BTNEN (44.7)	NC (26.3)	29.0	CO, H ₂ , Al ₂ O ₃	2250
BTNEN (38.0)	NC (22.6)	39.4	C, H ₂ , Al ₂ O ₃	2710
TNEOC (49.0)	NC (23.1)	27.9	CO, H ₂ , Al ₂ O ₃	2030
TNEOC (41.5)	NC (19.6)	38.9	C, H ₂ , Al ₂ O ₃	2580
TNEOC (59.7)	PNU XIII-A (12.0)	28.3	CO, H ₂ , Al ₂ O ₃	2110
TNEOC (50.4)	PNU XIII-A (10.2)	39.4	C, H ₂ , Al ₂ O ₃	2650

(a) Calculations based upon the water-arbitrary method described by Price (7).

Calculated heats of formation of HOX and polymer shown in Appendices I and II.

(b) Weight percent composition. NC = nitrocellulose, 13.4%N; PNU XIII-A = Aerojet-General polynitropolyurethane XIII-A

TABLE II
CALCULATED MAXIMUM SPECIFIC IMPULSE AS PROPELLANTS
OF SELECTED HOX/FUEL SYSTEMS

<u>Propellant System</u>	<u>I_{sp} (a)</u>	<u>$I_{sp} \cdot d^{(b)}$</u>
BTNEN/Al (73/27)	274	21.0
BTNEN/AlH ₃ (68/32)	318	21.4
AP/Al	269	
NC/NG/AP/Al	264	17.0 +

These calculations are those of the Allegany Ballistics Laboratory (10).

(a) $I_{sp} = \text{lbf-sec/lbw}$

(b) $I_{sp} \cdot d = \text{lbf-sec/in}^3$

TABLE III
APPROXIMATE VISIBLE SOLUBILITY LIMIT OF HOX'S IN
NITROPOLYMERS

Explosive Polymer	BTNEN		TNEOC		BTNEC		TEFO	
	Wt.%	Vol%	Wt%	Vol%	Wt%	Vol%	Wt%	Vol%
Nitrocellulose								
12.6%N	70	64.9	55	51.0	60	55.6	75	74.2
13.45%N	75	69.2	70	66.9	65	61.1	75	73.6
Polynitro- polyurethane (Aerojet XIII-A)	65	61.6	55	52.0	60	56.5	70	68.7
Polydinitro- propyl acrylate (Aerojet)	75	69.2	70	65.3	70	64.7		

Note: All values are subject to possible errors of $\pm 5\%$. These solubilities were measured by microscopic observation of the first appearance of crystals.

Below about 30% BTNEC no crystal diffraction could be observed. However, from 30% to the visual appearance of crystals at about 60%, crystallites appear in increasing amounts with increasing concentration which gave an X-ray pattern but were too small to be readily observed with a microscope. This view is supported qualitatively by the fact that densities of formulations in this range are intermediate between theoretical voidless densities calculated in two different ways. In one, the HOX is assumed to be in true solution in which case its liquid density is used. In the other it is calculated as a solid using the crystal density of the HOX. Impact sensitivities do not change a great deal with HOX concentration until the visual saturation level is exceeded when it becomes substantially more sensitive. The change in physical properties is substantial over this range.

Compatibility and storage life were judged by the 100°C vacuum thermal stability test. Provided all solvent had been removed, all of these systems were found to be satisfactory in gas evolution (<2.0 cc gas/g for 48 hrs.) with the exception of those formulations based upon BTNEN. This HOX is by far the best choice as an oxidant, thermodynamically, of the class, but its questionable thermal stability has long been recognized particularly when in solution or in the molten state (9). Therefore, BTNEN solutions balanced to the CO₂ level in guncotton grade NC, and PNU XIII-A were prepared and vacuum stability tests at 90°C measured both with and without added stabilizer. These samples were found to be generating brown fumes after about 8 weeks storage at ambient temperature. They produced 3-4 cc gas/g after only 1 hour at 90°C and over 30 cc gas/g in 18-24 hours in both stabilized (0.5% added 2,4-dinitrodiphenylamine) and unstabilized samples. Thus the stability is indeed quite poor by any standards, and it is considered unlikely that it would pass even propellant surveillance tests.

For nitrocellulose based formulations, the need for a stabilizer compatible with the HOX's posed a problem, as it was known that most explosives containing the -C(NO₂)₃ group were incompatible with the usual stabilizers such as diphenylamine and ethyl centralite. Using BTNEC for screening purposes, two compatible stabilizers have been found, 2,4-dinitrodiphenylamine and 4-hydroxybiphenyl. The latter represents a new class of phenolic stabilizers for nitrocellulose recently described by Frankford Arsenal (11) and others of this class would probably also be satisfactory.

Four processing methods were explored briefly with the following results:

(a) The simultaneous deposition of nitrocellulose or polynitro polyurethane and HOX from a common solvent by evaporation appeared to be satisfactory but suffered from the usual severe shrinkage. Such compositions extruded quite well or could be cast into sheets.

(b) Shock-gel precipitation developed at the Allegany Ballistics Laboratory (12) adapted to solutions of both polymer and HOX produced stable, gelled beads which conceivably could be stored and processed into form by compression molding or possibly solventless casting.

(c) Compression molding of shock-gelled beads of either nitrocellulose base or polynitro polyurethane base appeared quite promising provided sufficient plasticizing components were present. Temperatures of 65°-80°C and pressures of 15,000 - 25,000 psi produced tough, dense charges, capable of being machined but not brittle.

(d) Solventless casting was explored very briefly. The shock-gelled beads of nitrocellulose and HOX were swelled slowly by liquid explosive plasticizers such as the trinitroethyl esters of azelaic and sebacic acids or their mixtures with TEFO at 40-50°.

The sensitivity of these compositions was judged by drop weight impact sensitivity tests on 35 mg circular discs 4 mm in diameter. They were found to be comparable in sensitivity to double base propellants. In one gap sensitivity test a composition of 80% TEFO in 10% pyrocellulose plasticized with 10% chloroethyl phosphate was found to be considerably less sensitive than Composition A.

The only actual measure of performance has been a small scale fragmentation test of three compositions of BTNEC in PNU XIII-A. Performance comparable to Composition B was realized.

EXPERIMENTAL

In this preliminary study no attempt was made to do a complete development of techniques but merely to demonstrate their feasibilities and practicalities.

Source of Materials

The polynitropolyurethanes and polydinitropropyl acrylate were uncrosslinked linear polymers obtained from Aerojet-General Corporation, Azusa, California. PNU XIII-A was stated to have an intrinsic viscosity of 1.68 as a 1% solution in acetone at 25°. The two grades of nitrocellulose were production material from the Naval Propellant Plant, Indian Head, Maryland. The HOX's and nitroplasticizers were synthesized.

Processing Methods

Deposition from Solvent

This method was useful for preliminary screening purposes but required the time consuming removal of solvent later with the resultant final shrinkage. It would permit extrusion just prior to this final removal of solvent as an aid in fabrication of grains and mixing of ingredients. Several compositions were successfully extruded into 1/8" rods, but the ultimate size of the grains would be limited by this technique. As all of the polymers and HOX's used were soluble in acetone or ethyl acetate this was a convenient method. All components were dissolved at room temperature in the solvent with stirring at 25°-40°, followed by removal of solvent at 25° to a thick syrup and final evaporation in shallow trays. Last traces of solvent were removed by drying in a vacuum oven at 50°. Films of 1 to 5 mm thick were readily prepared but thicker films were difficult. These films were peeled out of the trays and examined under a low power (100X) microscope for crystallization and visually for flexibility and toughness. Circular pellets were cut from sheets of proper thickness with a cork borer to give 35 mg pellets 4 mm in diameter for impact sensitivity and thermal stability measurements(2). Densities were obtained by weighing a piece in water and air. This was found to be very dependent on removal of last traces of solvent. Some of the PNU and DNPA formulations were soft enough to be molded like stiff putty but after compression molding with heat these became much harder. Tables IV, V and VI show typical results of preparations of such films.

Dropping the acetone solution of a composition into water produced tough dense beads after drying, which if of the proper composition were then amenable to compression molding. However, the shock-gel solvents described below are much superior to acetone for nitrocellulose based compositions.

TABLE IV
CAST FILMS FROM ACETONE WITH NITROPOLYMERS

No.	Nitropolymer		HOX		Plasticizer Symbol	Metal Fuel	Density g/cc(a)	Impact Sensitivity (b)	Visible Crystals (c)	General Appearance
	Symbol	%	Symbol	%						
31B	DNPA	10	BTNEC	85	CEF		21 cm	Moderate	Stiff, translucent, putty	
32B	DNPA	12	BTNEN	80	CEF		15 cm	Moderate	Harder, translucent, putty	
32F	DNPA	12	TNEOC	80	CEF		25 cm	Moderate	Harder, translucent, putty	
26A	DNPA	20	TNEOC	80	None		29 cm	Slight	More flexible, tough	
26B	DNPA	20	BTNEC	80	None		37 cm	Slight	More flexible, tough	
18D	DNPA	14.5	TNEOC	56.7	TEFO			Slight	Stiff putty	
32C	PNU I-A	10	BTNEN	80	CEF		23 cm	Moderate	Some elasticity	
32G	PNU I-A	10	TNEOC	80	CEF			Moderate	Little elasticity	
32J	PNU I-A	12	TEFO	80	CEF		22 cm	Moderate	Stiff putty	
7B	PNU XIHA	17	TNEOC	80	CEF		25 cm	Slight on exterior only	Leathery	
8A-2	PNU XIHA	27.1	BTNEC	70	CEF		14 cm	Moderate	Translucent, tough, leathery	
14A	PNU XIHA	22	BTNEC	75	ETNB			Slight	Translucent, tough, leathery	
14B	PNU XIHA	22	BTNEC	75	CEF		1.69	Slight	Translucent, tough, leathery	
18C	PNU XIHA	14.1	TNEOC	57	TEFO		28.9	Severe	Soupy crystalline mush	
20E	PNU XIHA	67			TNEAz		33	None	Leathery, tough, elastic film can be creased and smoothed out	
25C	PNU XIHA	22	BTNEC	78			1.78	Moderate	Leathery, tough	
27B	PNU XIHA	17	BTNEC	83				Severe	Less flexible than 25C	
28A	PNU XIHA	33	BTNEC	67				None	Elastic, tough	
28B	PNU XIHA	55.7	BTNEC	44.3				None	Stiff chewing gum	
28C	PNU XIHA	35.0	BTNEN	65.0				None	Elastic tough	
29A	PNU XIHA	17.4	TNEOC	52.2	CEF		2.4	AI(28.0)	Some elasticity, fairly tough	
29B	PNU XIHA	16.2	BTNEC	53.6	CEF		2.1	AI(28.1)	Some elasticity, fairly tough	
32B-2	PNU XIHA							Moderate	Some elasticity, fairly tough	
32C-2	PNU XIHA	39.8	BTNEC	51.4	TEFO		8.8	None	Some elasticity, fairly tough	
32D-2	PNU XIHA	34.2	BTNEC	56.2	TEFO		9.6	None	Some elasticity, fairly tough	

CEF = β -Chloroethyl phosphate, Celanese Corporation.

(a) By weighing in water and weighing in air.

(b) NOL machine, 2.5 kg. weight on 35 mg pellets. JPN and AHH double-base propellants give values of 23 cm and 28 cm in this test.

(c) Via Microscope, 100X.

TABLE V

CAST FILMS FROM ACETONE WITH NITROCELLULOSE (13.45%N)

No.	%NC	HOX	%HOX	Plasticizer		Metal Fuel	Density g/cc(a)	Impact Sensitivity(b)	Visible Crystals(c)	General Appearance
				Symbol	%					
4C	16	TNEOC	75	CEF	9		14 cm	None	Translucent, brittle	
7A	27	TNEOC	70	CEF	3		16 cm	None	Clear, hard, brittle	
7D	16.2	TNEOC	52	CEF	6.5	Al(25%)	19 cm	None	Hard, tough, pliable	
17G	19.6	TNEOC	70	ETTNB	10		14 cm	None	Smooth, tough	
18B	27.2	TNEOC	48.3	TEFO	24.5		24 cm	None	Excellent clear tough film	
24A	28.2	TNEOC	53.5	TEFO	22.5			None	Clear sheet can be creased and smoothed out	
21A	20	TNEOC	70	TNEAz	10		1.68	Slight	Brittle, translucent	
21B	25	TNEOC	70	TNEAz	5		1.68	None	Brittle, clear	
21C	15	TNEOC	70	TNEAz	15			Slight	Somewhat flexible, translucent	
21D	25	TNEOC	60	TNEAz	15			None	Flexible, translucent	
24B	21.2	TNEOC	56.1	TEFO	17.1			None	Flexible, tough	
		TNEAz	5.6							
8B	17	BTNEC	80	CEF	3			Many	Crumbly, translucent	
8B2	27.1	BTNEC	70	CEF	2.9		15 cm	None	Clear, brittle	
17F	19.6	BTNEC	70	ETTNB	10			Slight	Wrinkles not so brittle	
21E	25	BTNEC	60	TNEAz	15			None	Flexible	
19D	27.2	BTNEC	48.3	TEFO	24.5			None	Wrinkled somewhat brittle	
4E	16	TNETB	75	CEF	9			Many	Crumbly, brittle, wrinkled	
4H	24.6	TNETB	67	CEF	8.4			Many	Crumbly, brittle, wrinkled	
20B	67			TNESeb	33		1.56			
20G	67			TNEAz	33					

CEF = β -Chloroethyl phosphate, Celanese Corporation.

(a) By weighing in water and weighing in air.

(b) NOL machine, 2.5 kg. wt. on 35 mg pellets. JPN and AHH double-base propellants give values of 23 cm and 28 cm in this test.

(c) Via Microscope 100X

Nitrocellulose was guncotton grade from production at Naval Propellant Plant, Indian Head, Md.

TABLE VI

CAST FILMS FROM ACETONE IN NITROCELLULOSE (12.60%N)

No.	%NC	HOX	%HOX	Plasticizer		Metal Fuel	Density g/cc(a)	Impact Sensitivity(b)	Visible Crystals(c)	General Appearance
				Symbol	%					
30A	7.5	BTNEC	85	CEF	7.5		18 cm	Some	Translucent, tough, leathery	
32A	10.0	BTNEC	80	CEF	10.0		36 cm	None	Decomposed at 25° in few weeks	
30B	10.0	BTNEC	55	CEF	10.0	Al(25%)	29 cm			
1A	27.0	TEFO	70	DBP	3		25 cm	None	Leathery	
32I	20	TEFO	80				14 cm	Many	Milky-translucent	
2A	22	TEFO	70	CEF	8		23 cm	None	Soft, leathery, tough	
7C	17.6	TEFO	56.0	CEF	6.4	Al(20%)	14 cm		Soft, tough	
1C	8.4	TNEOC	56.4	CEF	5.1	Al(30%)	26 cm			
1B	27.0	TNEOC	7.0	DBP	3			Many	Brittle	
17E	19.6	TNEOC	70	ETTNC	10			Some	Smooth tough film	
2B	35.0	TNEOC	60	DBP	5		25 cm	Some	Hard horny	
2C	28	TNEOC	60	CEF	12		29 cm	Some	Soft, pliable, tough	
22D	20	TNEOC	60	TNEAz	20				Flexible clear film with islands of crystals	
18A	24.1	TNEOC	50.4	TEFO	25.5			Some	Flexible, translucent	
32E	10.0	TNEOC	80.0	CEF	10		16 cm	Some	Flexible, translucent	
22A	20.0	BTNEC	70.0	TNEAz	10			Some	Crumbly, wrinkled, no strength	
22B	25.0	BTNEC	63.0	TNEAz	12			Some	Crumbly, some wrinkled	
22C	20.0	BTNEC	60.0	TNEAz	20			None	Smooth, no strength	
17C	20.0	BTNEC	70.0	ETTNC	10			None	Wrinkles	
31A	7.5	BTNEC	85.0	CEF	7.5		26 cm	Many	Stiff, leathery	
19C	24.1	BTNEC	50.5	TEFO	25.5		1.63	None	Smooth, stiff, leathery	
4A-2	24.6	TNETB	67.0	CEF	8.4			Many	Crumbly, wrinkled, poor strength	
15H	50.0	2,2-Dinitro-propanediol			50.0			Many		
20A	67			CEF	33		1.58	None	Transparent sheet can be folded and creased and crease smoothed out.	
15F	50			ETTNC	50			None	Transparent sheet can be folded and creased and crease smoothed out	
20C	67			TNESeb	33		1.56	None	Transparent sheet can be folded and creased and crease smoothed out	
15G	50			DNPF	50			Many	Brittle	
20F	67			TNEAz	33			None	Transparent sheet can be folded and creased and crease smoothed out	

(a) By weighing in water and then in air.

(b) NOL Machine 2 1/2 kg. weight on 35 mg pellets. JRN and AHH double-base propellants gave values of 23 cm and 28 cm in this test.

(c) Via Microscope 100X

CEF - β -Chloroethyl Phosphate-Celanese Corp.

DBP - Dibutyl Phthalate

Nitrocellulose was production material from Naval Propellant Plant, Indian Head, Md.

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Shock-Gel Precipitation of Nitrocellulose Formulations

This technique developed at the Allegany Ballistics Laboratory for double-base propellants (12) was found to be very useful for nitrocellulose based compositions, but for PNU based mixtures gave the same results as water precipitation from acetone. All components, HOX, stabilizer, NC, and plasticizer if needed, were dissolved in the proper shock-gel solvents and by drop-wise addition to water produce small spheres of gelatinized composition which when dried were much more amenable to compression molding. These spheres appear to be homogeneous and devoid of crystalline material provided the solubility limit was not exceeded by the composition. The mixtures of methyl cellosolve and propylene glycol recommended by the Allegany Ballistics workers appeared to be quite satisfactory for this method.

Casting and Plasticization

A brief search was made for a liquid or low melting solid explosive which would plasticize these polymers without detracting seriously from the oxygen content and which would be thermally stable and reasonably insensitive. The compounds examined are shown in Table VII. All but one appeared to plasticize well, but TNEAz and TNESeb were preferable to the ETNB, whose vapor pressure was too high. The TEFO appeared to be the best of all and had the added advantage of high density and oxygen content. It did not appear to sensitize formulations any more than would a corresponding amount of HOX.

Solventless casting techniques have been attempted in a preliminary way only. Dried nitrocellulose/HOX formulations, precipitated from acetone into water, were moistened with 10% liquid explosive plasticizers ETNB and TNEAz and allowed to stand for several days at 25° and 50°. Swelling and gelatinization occurred slowly and incompletely.

Compression Molding

This has been the most useful technique to date. It involved first the preparation of a molding powder by precipitation into water from acetone or a shock-gel solvent, followed by filtration and drying. This molding powder could be stored, and was readily compression molded at 60°-90° into tough, dense, machinable cylindrical shapes. By employing different plasticizer contents the hardness could be varied over a wide range. A tabulation of selected compositions is shown in Table VIII.

TABLE VII
POLY-NITRO PLASTICIZERS

Compound	Symbol	Formula	Density g/ml	M.P.	Impact (a) Sensitivity	Comments
Ethyl 4, 4-trinitrobutyrate	ETNB	$C_6H_9O_8N_3$	1.37	14°C	>300 cm	Plasticizes NC and PNU well, but has an appreciable vapor pressure.
bis(Trinitroethyl)sebacate	TNESeb	$C_{14}H_{20}O_{16}N_6$	1.34	42°C	>300 cm	Plasticizes NC and PNU well and is non volatile.
bis(Trinitroethyl)azelate	TNEAz	$C_{13}H_{18}O_{16}N_6$	1.43	23°C	90 cm	Plasticizes NC and PNU well and is non volatile.
2, 2-Dinitropropanediol	DNP	$C_3H_4O_6N_2$	1.65	65°C	>300 cm	Poor plasticizer with low solubility.
Trinitroethyl formal	TEFO	$C_5H_6N_6O_{14}$	1.73	65°C	7 cm	Plasticizes NC and PNU well and is non volatile.
2, 2-Dinitropropyl formal	DPFO	$C_7H_{12}O_{10}N_4$	1.57	32°C	183 cm	

(a) RDX = 22 cm, TNT = 180 cm

TABLE VIII

COMPRESSION MOLDING TRIALS

Sample No.	Composition		HOX	How Prepared	Molding Conditions		Density Observed	Appearance
	Polymer	Plasticizer			Pressure psi	Temp. °C		
32F	DNPA(12)	CEF(8)	TNEOC(80)	Acetone ppt. into H ₂ O	25,000	60	1.60	Fairly hard, extruded around ram at 80°
26B	DNPA(20)		BTNEC(80)	Acetone ppt. into H ₂ O	25,000	80	1.65	
14B	PNU XIII-A(22)	CEF(3)	BTNEC(75)	Acetone ppt. into H ₂ O	25,000	80	1.66	Fairly hard, machined well
14B	PNU XIII-A(22)	CEF(3)	BTNEC(75)	Rolled sheet	50,000	80	1.69	Extruded around ram at 100°
24A	GC(28.7)	TEFO(22.5)	TNEOC(53.5)	Shock gel	25,000	65	1.70	Fairly homogeneous, tough machinable
24B	GC(21.2)	TEFO(17.1) TNEAz(5.6)	TNEOC(56.1)	Shock gel	25,000	65	1.66	Fairly homogeneous, tough machinable
25B	PNU XIII-A(22)		TNEOC(78)	Acetone ppt. into H ₂ O	5,000	80-110	1.52-1.55	Striated-not homogeneous, crystals
25C	PNU XIII-A(22)		BTNEC(78)	Acetone ppt. into H ₂ O	25,000	80	1.78	Slight striations-hard, tough, machinable
25C	PNU XIII-A(22)		BTNEC(78)	Acetone ppt. into H ₂ O	50,000	65	1.73	Striated, non-homogeneous, tough, machinable
27B	PNU XIII-A(18)		BTNEC(82)	Acetone ppt. into H ₂ O	50,000	65	1.77	Striated, non-homogeneous, tough, machinable
28A	PNU XIII-A(33)		BTNEC(67)	Acetone ppt. into H ₂ O	50,000	65	1.72	Fairly homogeneous, machinable

Dwell times were 10-20 minutes.

In several cases where too high temperatures and pressures were employed for this molding, the material extruded around the ram of an old mold and it is believed that a solventless extrusion might be developed with these materials.

With synthetic polymers such as polydinitropropyl acrylate or the polynitropolyurethanes a desirable method might be the incorporation of the HOX during the polymerization in much the same manner in which ammonium perchlorate is introduced in current polyurethane based composite propellants. This has not been attempted. As the Aerojet-General workers have ascertained⁽¹³⁾ that trinitromethyl groups appear to be chain transfer agents in vinyl type (free radical) polymerizations, this may eliminate the acrylate derivatives from such consideration.

Extrusions

In addition to accidental extrusions of several preparations around the ram during compression molding trials at too high a temperature, Table VIII, three different compositions were successfully extruded with rather crude equipment. These are shown in Table IX. The samples were prepared by evaporation of an acetone solution to a rubbery sheet. This was cut into circular discs with a cork borer to fit the extrusion die. The press was a laboratory arbor press designed for the extrusion of metallic sodium. The orifice on the die was a 0.125" circular hole. The extrusion was easily carried out at 25° and the grains dried in a vacuum oven at 40-50° for final removal of solvent. All samples retained their shape after drying but some shrinkage was noted with all of them.

Thermal Stability

The vacuum thermal stability test⁽²⁰⁾ was employed generally at 100°C for 48 hours as an accelerated surveillance, storage and compatibility test. Volumes of evolved gas of less than 2.0 cc/g are believed to represent very satisfactory stability. Values from 2.0 to 6.0 cc/g are barely satisfactory and these samples require further evaluation, and volumes above 6.0 cc/g are generally indicative of poor stability. Selected compositions of each type composition only are shown in Table X, as variations in the amounts of each component produced only minor variations.

TABLE IX

EXTRUSIONS
(1/8" orifice)

No.	HOX	Polymer	Plasticizer	Remarks
15A	BTNEC (75)	PNU XIII-A (22)	CEF (3)	Extruded well
15B	BTNEC (75)	PNU XIII-A (22)	MTNB*(3)	Extruded well
15C	BTNEC (75)	NC (22)	MTNB*(3)	Extruded well

Note: The samples still contained acetone as solvent. The press used was a laboratory arbor press used for extrusion of metallic sodium. The temperature was about 25°.

* MTNB = Methyl 4, 4, 4-trinitrobutyrate

TABLE X

VACUUM THERMAL STABILITIES

No.	Polymer	HOX	Plasticizer	Metal Fuel	Test Temp(°C)	Time (hrs)	cc gas/ evolved
As received	NC				100	48	0.30
	GC				100	48	0.80
24A	NC	BTNEC			100	48	4.6
18A	GC	TNEOC	TEFO		100	48	0.74
2B	NC	TNEOC	TEFO		100	48	6.8
30B	NC	TNEOC	CEF+DBP		100	48	7.2
28C	GC	BTNEN			90	1	3.5
26A	PNU XIII A	BTNEN			90	1	4.5
26B	DNPA	TNEOC			100	48	1.97
27B	DNPA	BTNEC			100	48	3.3
25C	PNU XIII A	BTNEC			100	48	4.6
28A	PNU XIII A	BTNEC			100	48	3.7
29A	PNU XIII A	TNEOC	CEF	Al	100	48	7.4
29B	PNU XIII A	BTNEC	CEF	Al	100	48	6.0
							5.8

Stabilizers

BTNEC	Ethyl Centralite	100	6	>30
BTNEC	2, 4-Dinitrodi-phenylamine	100	48	1.6
BTNEC	p-Hydroxydi-phenyl	100	48	1.8

Notes: Proportions are not included as they had only minor effects on results. Results are sensitive to traces of residual solvent.

CEF = β-Chloroethyl Phosphate

DBP = Dibutyl Phthalate

Et Centralite = Sym. Diethyldiphenylurea

NC = Pyrocellulose (12.60%N)

GC = Guncotton (13.45%N)

PNU XIII-A = Polynitropolyurethane

DNPA = Polydinitropropyl acrylate

See Appendix 2

As an additional test, the hot bar ignition temperature test⁽²⁰⁾ was applied to representative compositions and is shown in Table XI together with the explosive PBX-9404 (see glossary) and experimental propellants from Aerojet and the Rohm and Haas Laboratories consisting of AP in a polynitro matrix.

Nature of Solution

In attempting to calculate voidless densities and compare observed values of both films and compression molded specimens it became apparent that the latter values were higher than those calculated from the liquid densities of all components, but lower than values calculated using the crystal densities of all components. Typical calculations are shown in Table XII. It was concluded that a portion of the solid components is in true solution where liquid densities would be proper, and a portion is in the form of sub-microscopic crystallites where crystal densities would be appropriate. The X-ray diffraction examination of compositions of PNU-XIII-A and BTNEC in various proportions was performed to clarify this point. The polymer has no crystalline character or diffraction pattern of its own so that the known diffraction bands of crystalline BTNEC were readily observed. The results are shown in Table XIII.

TABLE XIII

X-RAY DIFFRACTION EXAMINATION OF SYSTEM: PNU/ BTNEC

Wt. % BTNEC	Wt. % PNU XIII-A	X-Ray Diffraction Pattern
0	100	None
10	90	None
25	75	None
40	60	Weak BTNEC
55	45	Moderate BTNEC
65	35	Strong BTNEC

TABLE XI
IGNITION TEMPERATURES

No.	Composition	Ignition Temperature °C
29A	TNEOC/PNU XIII-A/Al/CEF 52.2/17.4/28.0/2.4	No ignition <375
29B	BTNEC/PNU XIII-A/Al/CEF 53.6/16.2/28.1/2.1	200-213
25C	BTNEC/PNU XIII-A 78/22	203
24A	TNEOC/TEFO/GC 51.0/21.5/27.4	184
	PBX 9404 (see glossary)	272
L5265 (Aerojet)	AP/PNU XIII-A 82/18	232
QR (Rohm and Haas)	Poly-Petrin Acrylate 14.6 AP 47.9 TEGN 17.5 Ethyl Centralite 0.2 Al 18.0 EHM Monomer 1.6 Polyester Crosslinker 0.25	192

TABLE XII
COMPARISON OF CALCULATED VS. OBSERVED DENSITIES

Composition No.	Components	Composition (Wt. %)	Component's Voidless Densities		Observed Density of Cast Films	Calculated Voidless Density	
			As Solids	As Liquids		HOX As Solid	HOX As Liquid
	Pyrocellulose	67	1.57				
	Chloroethyl phosphate	33		1.43	1.58		1.52
	Guncotton	67	1.60				
	TNESeb	33		1.37	1.56		1.52
	Pyrocellulose	67	1.57				
	TNEAz	33		1.43	1.56		1.52
21A	Guncotton	20	1.60				
	TNEOC	70	1.84	1.66(a)	1.685	1.73	1.62
	TNEAz	10		1.43			
18B	Guncotton	27.2	1.60				
	TNEOC	48.3	1.84	1.66	1.62	1.74	1.62
	TEFO	24.5	1.73	1.56(a)			
19C	Pyrocellulose	24.1	1.57				
	BTNEC	50.4	1.88	1.69(a)	1.63	1.76	1.63
	TEFO	25.5	1.73	1.56			
25C	PNU XIII-A	22	1.63				
	BTNEC	78	1.88	1.69(a)	1.77(b)	1.82	1.68
26B	DNPA	20	1.48				
	BTNEC	80	1.88	1.69(a)	1.65(b)	1.78	1.64

(a) Estimated as 10% less than crystal density.
(b) Pressed

By comparison with the visual solubility limit of this system from Table III it is apparent that below about 30% the BTNEC is in true solution but that between 30% and 60%, where crystals finally become visible with the microscope, a steadily increasing appearance of diffraction bonds suggests sub-microscopic crystallites. This raises the question of possible further slow crystallization during storage. A 24 hour storage of two nitrocellulose compositions, a PNU and a DNPA composition at -70°C failed to alter the microscopic appearance of the sample but the above X-ray specimens are being stored at ambient temperature and will be re-examined after one year.

Fragmentation Test

This is the so-called plate-push test developed at NOL⁽¹⁹⁾ which has been scaled down to charges 0.37 inches by 1.0 inches long at the Lawrence Radiation Laboratory. As only small amounts of explosive are required it is useful as a screening test. However, the time available for energy release is only 2-5 μsec. The samples were prepared by compression molding 0.5 x 1.0" pellets and machining them down to the required diameter. The system BTNEC/PNU XIII-A was chosen and three different oxygen levels prepared. All exceeded the saturation level of BTNEC and contained some visible crystalline BTNEC, but had impact sensitivities in the usual range of 20-35 cm. The results are shown in Table XIV.

TABLE XIV
SMALL SCALE PLATE-PUSH TEST

No.	Composition		Density (g/cc)	Oxygen Balance (Ratio CO ₂ /CO)	Relative Plate Velocity ^(a)
	%BTNEC	%PNU XIII-A			
25C	78	22	1.74	5/1	1.21
28A	67	33	1.71	1/1	1.27
27B	82	18	1.78	1/0	1.31
PBX					
9404			1.82		1.38
TNT			1.63		1.00

(a) Relative to TNT as 1.00

Gap Sensitivity Test

The small scale gap test developed at NOL was employed. The formulation tested was TEFO/NC/CEF (80/10/10) which had a pellet impact sensitivity of 18 cm. Lead azide was used as the donor explosive. With six trials at zero gap, two detonated and two deflagrated giving no plate dent. With an air gap about half that required for 50% initiation of Composition A, two samples deflagrated and four failed out of six trials. Thus it was concluded that this composition, which was one of the more sensitive ones to impact and exceeded the solubility limit for TEFO, was very much less sensitive to the gap test than Composition A.

CONCLUSIONS

The preparation of an essentially homogeneous plastic matrix rich in nitro group oxygen which would be sufficiently safe for practical military use in handling and storage appears to be quite feasible. The use of this matrix with energetic fuels such as aluminum powder to formulate either high explosives or energetic solid propellants offers real promise. For high explosives, this matrix with its very high oxygen content would permit the use of a high percentage of aluminum and still maintain the optimum Al/O ratio for producing explosives with substantially increased explosion energy for either airblast or underwater applications. An energy increase of 25% over either H-6 or HBX-3 appears quite possible with a substantial part of it in shock energy. For solid propellant applications these formulations may well provide a specific impulse as high as 265 and would contain only the suspended aluminum powder as a separate solid phase, thus giving much better control of physical properties and burning rates. These propellants while probably safe enough for military use in storage and handling might well be capable of mass detonation if explosively boosted. This disadvantage is believed inevitable in all propellant formulations in which, in order to obtain high energies, all components are of an energetic nature. However, if the compositions are as safe as the more insensitive warhead explosives their practical use should be possible.

RECOMMENDATIONS

It is recommended that this promising development be actively pursued along the following lines:

- (a) A more accurate assessment of sensitivities by the regular card-gap test;
- (b) Actual performance measurements of the optimum formulation as an underwater explosive with careful measurement of the energy distribution between shock and bubble;
- (c) Actual performance measurements of the optimum formulation as a solid propellant both as to burning rates and specific impulse;
- (d) Development of practical processing techniques for loading into large irregularly shaped spaces preferably without the use of high pressures. This may be possible by introducing a partially polymerized composition into a space followed by a heat cure to complete the polymerization;
- (e) Continued study of the effect of composition on physical properties, sensitivity and processing methods;
- (f) The use of other nitropolymers such as petrin acrylate or nitrocellulose cross-linked with a diisocyanate or a diacid anhydride. The cross-linked nitrocellulose which has been investigated briefly by the Allegany Ballistics Laboratory and Ballistics Research Laboratory appears particularly promising as it seems to greatly improve the heat stability without detracting too seriously from its desirably high oxygen content. The combination of polymerization of monomers and blending of HOX into one step seems worth investigation.

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APPENDIX I

HIGH OXYGEN EXPLOSIVES, HOX's

Name and Symbol	Chemical Structure	Empirical Formula	Molecular Weight	Melting Point, °C	Crystal Density	Impact Sensitivity ^(a)	Calc. Heat of Formation (kcal/mol) ^(b)	Oxygen Content ^(c)	
								CO level	Above CO ₂ level
bis(Trinitroethyl) nitramine (BTNEN)	$[\text{C}(\text{NO}_2)_3\text{CH}_2]_2\text{NNO}_2$	$\text{C}_4\text{H}_4\text{N}_8\text{O}_{14}$	388	94	1.96	10 cm	+ 12	48.5	97
Trinitroethyl orthocarbonate (TNEOC)	$[\text{C}(\text{NO}_2)_3\text{CH}_2\text{O}]_4\text{C}$	$\text{C}_9\text{H}_8\text{N}_{12}\text{O}_{28}$	732	169	1.84	8 cm	-183	48.8	122
bis(Trinitroethyl) carbonate (BTNEC)	$[\text{C}(\text{NO}_2)_3\text{CH}_2\text{O}]_2\text{CO}$	$\text{C}_5\text{H}_4\text{N}_6\text{O}_{15}$	388	117	1.88	16 cm	-167	48.5	129
Trinitroethyl formal (TEFO)	$[\text{C}(\text{NO}_2)_3\text{CH}_2\text{O}]_2\text{CH}_2$	$\text{C}_5\text{H}_6\text{N}_6\text{O}_{14}$	374	65	1.73	8 cm	-103	62.3	374
Trinitroethyl orthoformate (TNEOF)	$[\text{C}(\text{NO}_2)_3\text{CH}_2\text{O}]_3\text{CH}$	$\text{C}_7\text{H}_7\text{N}_9\text{O}_{21}$	553	128	1.80	8 cm	-140	52.6	158
Nitroglycerine (NG)	$\text{O}_3\text{NCH}_2\text{CH}(\text{NO}_3)\text{CH}_2\text{NO}_3$	$\text{C}_3\text{H}_5\text{N}_3\text{O}_9$	227	13	1.60 (liquid)	4 cm	-113	64.8	454
Lithium Perchlorate (LP)	LiClO_4	LiClO_4	106	236	2.43	Not explosive	-106	26.5	26.5

(a) NOL PETN = 13 cm, RDX = 22 cm.

(b) A positive value is an endothermic value.

(c) Grams required to produce one surplus gram/atom of oxygen above the level indicated.

APPENDIX II

NITROPOLYMERS

Name and Symbol	Polymer Unit Empirical Formula	Voidless Density	Unit Molecular Weight	Unit Calculated Heat of Formation	CO level	Added Oxygen Required (a) CO/CO ₂ I/I	CO ₂
Nitrocellulose 12.60%N (Pyro)	C ₆ H ₇ N _{2.5} O ₁₀	1.57	274	-160	-0.5	2.5	5.5
Nitrocellulose 13.45%N (GC)	C ₆ H ₇ N _{2.77} O _{10.5}	1.60	287	-142	-1.0	2.0	5.0
Polydinitropropyl acrylate (DNPA)	C ₆ H ₈ N ₂ O ₆	1.48	204	-127	4.0	7.0	10.0
Polynitropolyurethane I-A (PNU I-A)	C ₅ H ₇ N ₃ O ₆	1.57	205	-100	2.5	5.0	7.5
Polynitropolyurethane XIII-A (PNU XIII-A)	C ₉ H ₁₄ N ₆ O ₁₂	1.63	366	-164	4.0	8.5	13.0
Polypetrin acrylate (PPA)	C ₈ H ₁₁ N ₃ O ₁₁		325	-220	2.5	6.5	10.5

(a) g/atoms of oxygen required per polymer unit for the level indicated.

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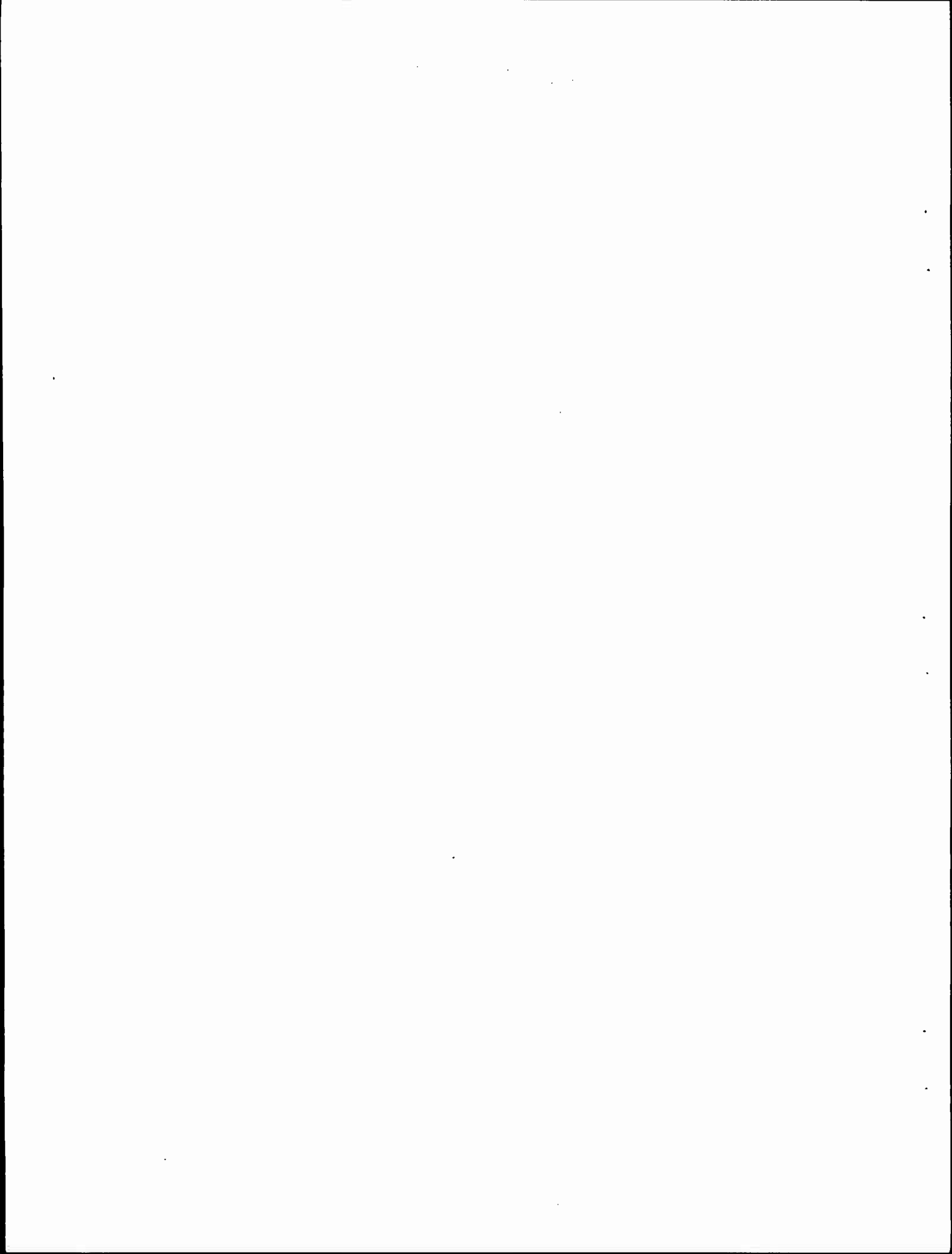
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