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THIS PAPER presents a status report on the work done under a contract on fuel emulsions funded by the Army. This work is involved with the development of a fuel emulsion for use in helicopters which minimizes the hazards associated with liquid fuel. Other approaches to thickening fuels will be discussed as will be some of their more important disadvantages.

Liquid fuels, in the form of turpentines, vegetable or other fatty oils, and crude petroleum have been available during most of recorded history, and have generally suffered from a well-earned reputation for danger. The very phrase "blazing oil" brings an echo of the fear which these otherwise admirable materials have inspired, with their tendencies to spill and flare up. There must have been many attempts to combine the security of the old solid fuels with the adaptability of the liquids by thickening the latter to produce a safety fuel. Unfortunately, the results achieved by such experimenters have not been very impressive.

A second group, with rather different objectives, has been much more successful in thickening liquids for use in flame

weapons. The spectacular results, from Greek Fire to Napalm, are well known; what is not obvious is that the two groups have been using the same basic principles for control of the flashing and spreading tendencies of the liquid fuels, and that some of the weapons techniques are adaptable to the safety problem. The authors are very fortunate to be part of the first program which is aimed at such application of these techniques and which has been funded on a scale comparable to that of the weapons development activities. The incentive arises primarily from the vulnerability of helicopters and other transport vehicles to projectiles in Viet Nam. A significant proportion of the casualties are due to fires from our own fuel which is being ignited by ground fire or crash.

In Table 1, some of the goals of the weapons and safety fuel developers are shown. As shown, there are conflicts of interest; there are also conflicts between two weapons groups, and there are points of unanimity (such as maximum heat of combustion) which are not included. The real problem areas are those labeled "optimize," since this represents an

ABSTRACT

The current incentive for safety fuels is due to excessive loss of aircraft in Vietnam due to fires. Evaluation of four classes of thickened fuels eliminates "canned-heat" gels, the visco-elastic Napalm type, and the polymer-thickened fluids. Emulsions-thickened fuels seem more compatible with aircraft systems. Points of superiority include ease of removal from tanks, good atomizing properties in engines, and constancy of rheological properties over a wide temperature range.

Recent work on an Army-sponsored contract to develop emulsion safety fuels for Army helicopters and cargo planes has uncovered a number of formulations containing at least

97% fuel. Based on early laboratory data, these emulsions appear to have good stability at -30 to 130 F. The separation of JP-4 varies from 1-10% after several cycles of heating and cooling between these limits.

One nonaqueous emulsion, WS-X-7063, has provided valuable background information. The yield stress of the emulsion can be varied 1000-3500 dynes/cm² by varying the ratio of continuous phase to emulsifier. Its performance characteristics in various engine fuel systems are under investigation. We hope the information produced will enable us to develop a fuel acceptable for use in selected military applications.

internal conflict. For example, the incendiary needs to spread his fuel to obtain a 5 minute burn, as a shorter time tends merely to singe the target and a longer time to decrease the flame height to an ineffective level. The safety man has the largest number of compromises to make as the engine must approximate normal liquid combustion while the personnel should be exposed to something comparable to burning wood or coal.

The four thickening techniques inherited from the weapons (and older safety fuel) work are as follows:

1. Gels, held together by the crystallization of soap-like materials (Fig. 1). These date back to Greek Fire, though modern formulations are far more sophisticated. In general, they resemble "canned-heat" in properties, though they can be made ashless. Since the gelling action depends on the adhesion of the elongated crystals to each other, and this adhesion is strongly affected by temperature, gels tend to become excessively stiff when cold and thin out when warm. They also adhere to tank walls, and are difficult to pump out cleanly unless follower plates are used as in grease guns. This kind of thickness lies mainly in a property known as "yield stress," representing the minimum pressure difference (measured under standard conditions) to initiate flow (Fig.

2). This is the parameter which is affected by temperature and which leads to poor discharge from tanks. The weapons use of gels essentially ended with the opening of World War II.

2. Pastes, in which the soap-like crystals are replaced by a preformed powder such as sawdust or silica gel. Two variables are the porosity and particle size of the powder. An interesting special case is micro-encapsulated fuel, in which the solid is formed around droplets of the fuel. Such products are too rigid to flow -- but the pastes which can be made to flow have essentially the same properties as the gels. The pastes have been more prominent in civilian safety fuels (that is, charcoal lighter) than in weapons.

3. Polymer Dispersions, resembling rubber cements, have a completely different structure (Fig. 3). Here the thickener has a length diameter ratio in the thousands or millions, compared to very low ratios for pastes and ratios of about 50-200 for gels. As a result, the whole nature of the thickening is different, and these fuels have no yield stress. When left undisturbed they flow down, like any ordinary liquid, to a perfectly flat surface. Under very mild agitation, they appear to be merely more viscous than the base fuel -- but with more intense agitation, an "elastic" component appears. The results must be seen to be appreciated; they include these "visco-elastic" fluids climbing up a rotating shaft or exerting a "normal" (meaning at a right angle to the plane of rotation) force on a disc which prevents such a climb. After rotation ceases, these fluids tend to unwind

Table 1 - Goals of Fuel Thickening

Property	Incendiary	Flame Thrower	Aircraft
Ease of ignition	H	H	O
Burning rate	O	O	O
Propagation of flame	H	H	L
Atomization	L	L	O
Spreading of fuel	O	H	L
Discharge from tanks	-	H	H
Ash content	-	-	L

H = Maximize
 L = Minimize
 O = Optimize
 - = Not important

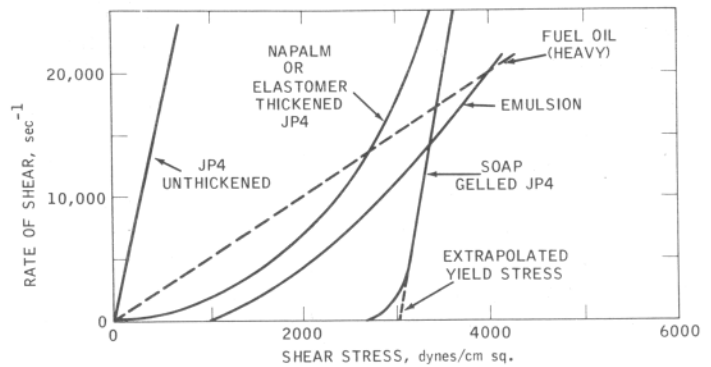


Fig. 2 - Flow of thickened fuels

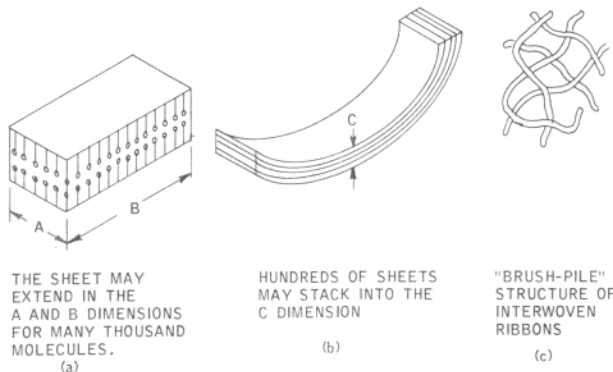


Fig. 1 - Soap-type gels

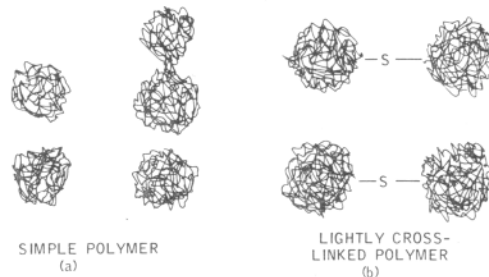


Fig. 3 - Elastomer thickened fuel structure

like a spring. When projected from a nozzle, the fuel rod diameter is larger than the opening. A third effect is "stringiness." These fuels tend to pull out into long filaments which snap back on breaking. Had not the rubber shortage forced further development, World War II incendiaries would have used these fluids. They are not, however, easy to discharge from tankage; their flame thrower performance would be mediocre (Table 2).

Two interesting variations are possible. In one, a light cross-linking is added by vulcanization, thus doubling or tripling the molecular weight. In another, a visco-elastic fluid is gelled essentially to combine the properties of viscosity, elasticity, and yield stress. A fuel of this type became standard for the 100 lb M-47 incendiary bomb, which requires extra tough fuel to resist atomization.

The temperature properties of the fuel depend to a remarkable extent on those of the polymer, once a certain degree of thickening is reached (a function of both concentration and molecular weight). While not all authorities agree with this description, such fuels resemble a polymer swollen with imbibed fluid much more than a dispersion of polymer in fluid. Those made from temperature insensitive polymers such as polybutene are insensitive -- but those made from polystyrene (Napalm B) are very sensitive to changes in temperature.

4. Napalm "M" thickened fuels represent an extension of the polymer class, but they are sufficiently different to warrant a class of their own.

(a) The backbone is composed of aluminum and oxygen atoms in an arrangement which appears to be held together mainly by hydrogen bonds, as the three valence-bonds of aluminum do not suffice (Fig. 4).

(b) Polymerization is spontaneous -- and reversible. Ordinary polymers show a permanent decrease in molecular weight on mechanical shearing, but Napalm M does not.

(c) The elasticity is far greater than with the polymers (Fig. 5).

(d) The fuel is so cohesive that it pulls loose from tank walls and discharges well even from complex systems.

The organic radicals can be varied widely. Grades M-1 and M-2, the original World War II versions, contained a mixture of naphthenic, coconut, and oleic acids (the name stems from Naphthenic and PALM oil) while the more modern M-4 contains synthetic octanoic acid. The latter appears

to have nearly all the properties desired by the weapons people -- but is so resistant to atomization as to be totally impractical for engine use. It is also the most difficult to ignite of all fuels; the means employed are burning magnesium sparks, (M-69), white phosphorus (M-47), a pyrotechnic flare cartridge (portable flame thrower), or a gas-oline blow torch (mechanized flame thrower).

Thus, the legacy from past work could not have been applied to aircraft safety with any real hope of success. Many parts of it, however, have indirect application. One may cite the technology of preparing thickened fuels in the field, handling them through fuel systems as complex as that on the helicopter, and testing them on both the laboratory and field levels. However, the fuel which now appears to be outstanding falls into a fifth class.

5. Emulsions are essentially different from the other classes, as they consist mainly of two immiscible liquids combined to make a product paradoxically resembling a gel. Of course, a third ingredient is required -- the emulsifier -- but this is usually a liquid also. The structure is shown schematically in Fig. 6A. Since no good photomicrographs of an emulsion of this type have yet been achieved, Fig. 6B represents the nearest equivalent, a closed-cell foam.

The mode of creating a yield stress from two liquids may be described by the following analogy: take some lead shots, to represent the spherical drops usually present in dilute emulsions such as milk. Compress these in a sleeve, by piston pressure, until only about 3% of voids remain. Then slide out the product gently; it will stand alone, since the spheres have become (roughly) dodecahedra. However, with some

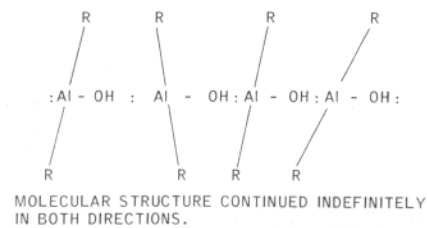


Fig. 4 - Napalm structure

Table 2 - Performance of Flame Thrower Fuels Compared

Gelling Agents			
Property	% Flashing	% Discharge	% Ash
Soap type	30-50	15-30	0-1.0
Elastomer	20	80	0
Napalm	10	95	~0.3
Emulsion	<50	>80	0-0.1

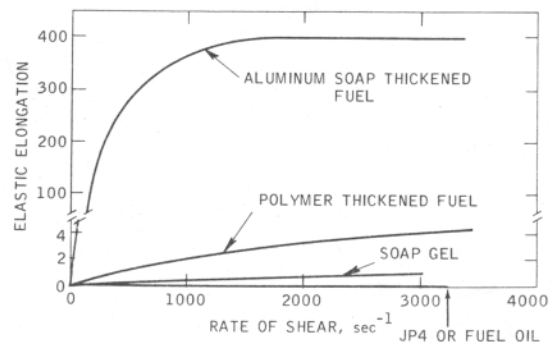


Fig. 5 - Effect of visco-elasticity

side ways force, the composite cylinder can be made to "flow" by spilling out as individual particles. This last example is not a good analogy since an emulsion with 97% of disperse phase flows by another mechanism. The dodecahedra elongate in the direction of the shearing force into the shape of prisms, lying with parallel axes, which can slide on one another. Up to a moderate rate of shear, the emulsifier can shift to accommodate the increase in area, but beyond this limit (about $10,000 \text{ sec}^{-1}$) coalescence starts to take place. At very high shear rates (over $100,000 \text{ sec}^{-1}$) up to 85% of the dispersed phase is set free.

This unique flow behavior leads to the second paradox of these fuels -- they are difficult to ignite when stationary, but burn like liquid after strong shearing. In a turbine engine-fuel system, the emulsion is sheared as it passes through the nozzle. Since the engine deals largely with a de-emulsified fuel, it is conceivable that engine performance will be close to normal.

In summary, emulsions as fuels appear to offer several important advantages over gelled fuels. Fuel emulsions are more easily atomized than gelled fuels because of breakdown to two liquids after severe shearing (about $10,000 \text{ sec}^{-1}$). Under similar conditions a gelled fuel is broken down

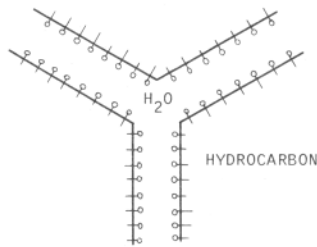


Fig. 6A - Emulsion-gel structure

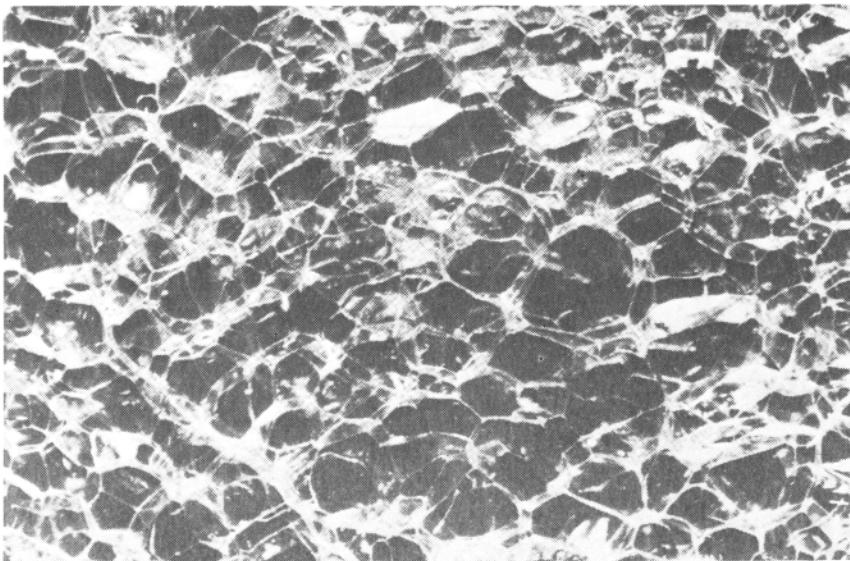


Fig. 6B - Foam structure

mainly into a solid containing entrapped liquid plus a quantity of free liquid, which is more difficult to atomize than two liquids. Because emulsions do not tend to wet certain surfaces, they are more easily expelled from tanks than are gels. Finally, the flow properties of an emulsion are not significantly affected by temperature because they are due to a physical packing of particles rather than any interactions between particles as is the case with gels. Because of this the flow properties of a fuel emulsion will be essentially the same between -20 and 130 F . This is not the case with gels.

Our company is presently working on an Army-sponsored contract to develop fuel emulsions that can be used in Army aircraft engines (principally helicopter engines) employed in combat areas. These fuels will be burned directly in engines. Basically, fuel emulsions must meet almost all the requirements of liquid fuels. In addition, they must be stable under a variety of conditions and have yield stresses greater than 1000 dynes/cm^2 . The latter represents a compromise which minimizes the difficulty of expelling such fuels from tanks and at the same time provides the required safety margin. A fuel emulsion having a yield stress of 1000 dynes/cm^2 should not flow from a hole caused by a 50 caliber bullet nor should it be atomized by the force of an 80 mph impact. In commercial fixed-wing aircraft, where the force of impact will be much greater, it is quite probable that higher yield stress emulsions will be required to prevent atomization of the fuel. (Fig. 7)

The principal characteristics that a fuel emulsion must possess for use in Army aircraft (principally helicopters) are summarized below:

Composition - Contain at least 97% of the fuel or its equivalent.

Stability -

1. Stable at room temperature for at least 30 days.
2. Stable at -20 F and up to 130 F . (Desired: stable at -65 F and up to 160 F .)

3. Stable under a gravitational force of 500 g.
4. Stable with respect to vibration (2 g force for 24 hr).

Corrosion - Must be compatible with general materials of construction.

Flow Properties - A yield stress $> 1000 \text{ dynes/cm}^2$.

Prior to our work, the emulsified fuels in the field had a number of deficiencies. These emulsions showed deficiencies with respect to shelf life, temperature stability, the nature of the continuous phase, and compatibility with practical materials of construction.

Our experimental approach has been to pin down the hydrophile/lipophile balances, solubility parameters, and hydrogen bonding parameters that are necessary to produce emulsions having the required stability and viscosity. Using this approach, we have prepared a number of emulsions in the HLB range of 11-14 that contain 3% emulsifier plus continuous phase. The maximum amount of water in these emulsions is 0.5-0.80%. The stability of these emulsions is good (Table 3) based on emulsions prepared in our laboratory with only about 5-15% separation of the JP-4 at 130 F and no separation at either room temperature or -20 F. These emulsions meet most of the Army's principal requirements for an emulsified safety fuel (Table 4), and they have yield stresses in excess of 1000 dynes/cm^2 . In addition, the gross heat of combustion of these emulsions is not significantly different from that of JP-4.

In addition to the preparation of stable emulsions containing water, we have prepared in our laboratory a series of completely nonaqueous emulsions which contain 97-98% JP-4, are almost transparent, have not shown any signs of instability at room temperature after more than a month of storage, have shown no instability after several freeze thaw cycles from -20 F to room temperature, separate only 1-2%

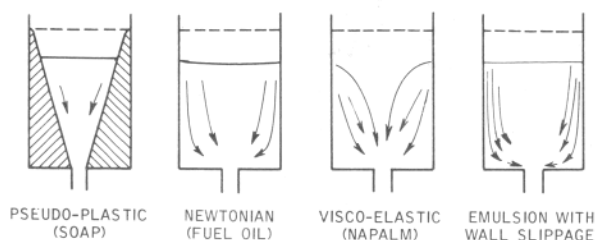


Fig. 7 - Discharge of thickened fuels from tanks

Table 3 - Typical Stability of Aqueous Fuel Emulsion

	% Separation
30 days at room temperature	0.0
Six, 6-hr cycles at 130 F	5-15
Six, 16-hr cycles at -20 F	0.0
1/2 hr centrifugation at 500 g	0.0

of JP-4 after several 6 hr cycles between room temperature and 130 F, and have exceptionally high yield stresses ($1000-3500 \text{ dynes/cm}^2$). (These data are summarized in Table 5 and 6.) The small separation of JP-4 at the higher temperature does not seem to be a problem since mild agitation reconstitutes the fuel emulsion, and under practical conditions, this may not be observed at all. The other principal properties of these emulsions are shown in Table 6.

The safety aspect of fuel emulsions can be demonstrated in part by their flow properties (specifically their yield stresses), evaporation rates, and flame propagation rates. As

Table 4 - General Physical Data on Aqueous Fuel Emulsion

Test	Emulsion	JP-4
Heat of combustion, Btu	19,600	20,345
Ash content, ppm	< 0.005	< 0.005
Four ball wear, mm	0.58	0.45
Reid vapor pressure	1.8	2.3
Yield stress, dynes/cm^2	1225	0.0
Corrosion of		
Al	none	none
304 Stainless	none	none
Titanium alloy	none	none
Copper, bronze	none	none

Table 5 - Typical Stability of Nonaqueous Fuel Emulsion

	% Separation
30 days at room temperature	0.0
Six, 6-hr cycles at 130 F	2.0
Six, 16-hr cycles at -20 F	2.0
1/2 hr centrifugation at 500 g	0.0

Table 6 - General Physical Data on Nonaqueous Fuel Emulsion

Test	Emulsion	JP-4
Heat of combustion, Btu	19,654	20,345
Ash content, ppm	< 0.005	< 0.005
Four ball wear, mm	0.73	0.45
Reid vapor pressure	1.9	2.3
Yield stress, dynes/cm^2	1900	0.0
Corrosion of		
Al	none	none
304 Stainless	none	none
Titanium alloy	none	none
Copper, bronze	slight*	none

*Inhibited by commercial inhibitors.

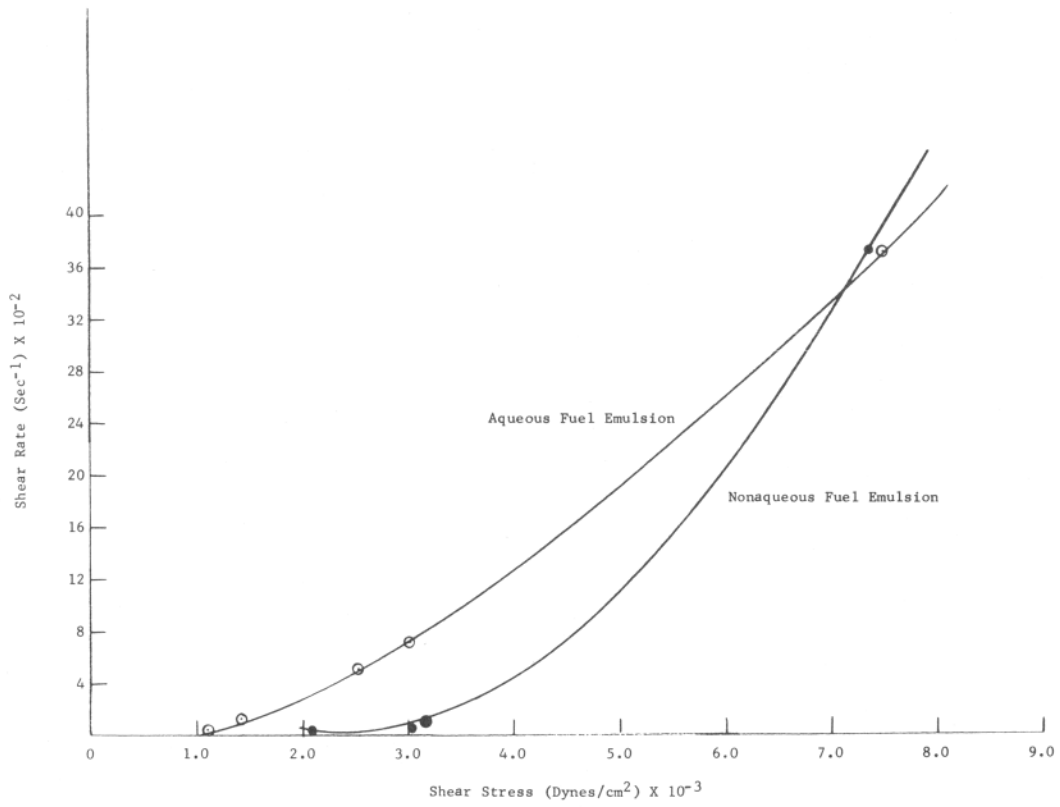


Fig. 8 - Flow properties of aqueous and nonaqueous fuel emulsion

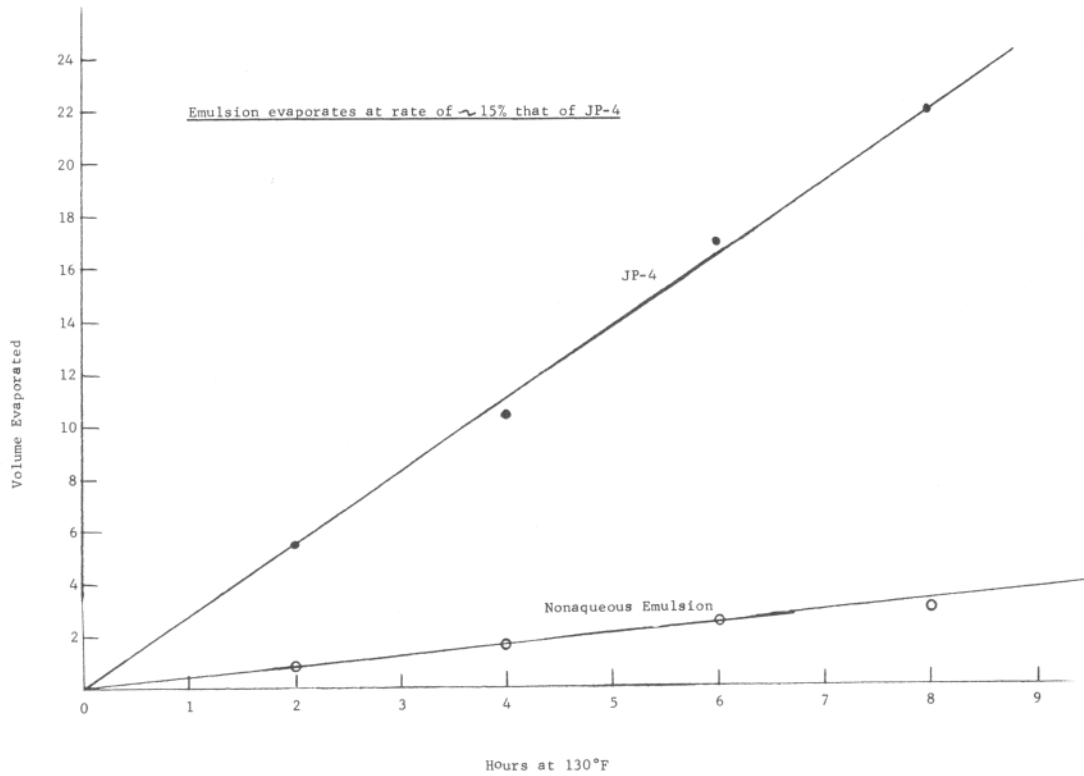


Fig. 9 - Evaporation of JP-4 and JP-4 emulsions under static conditions at 130 F

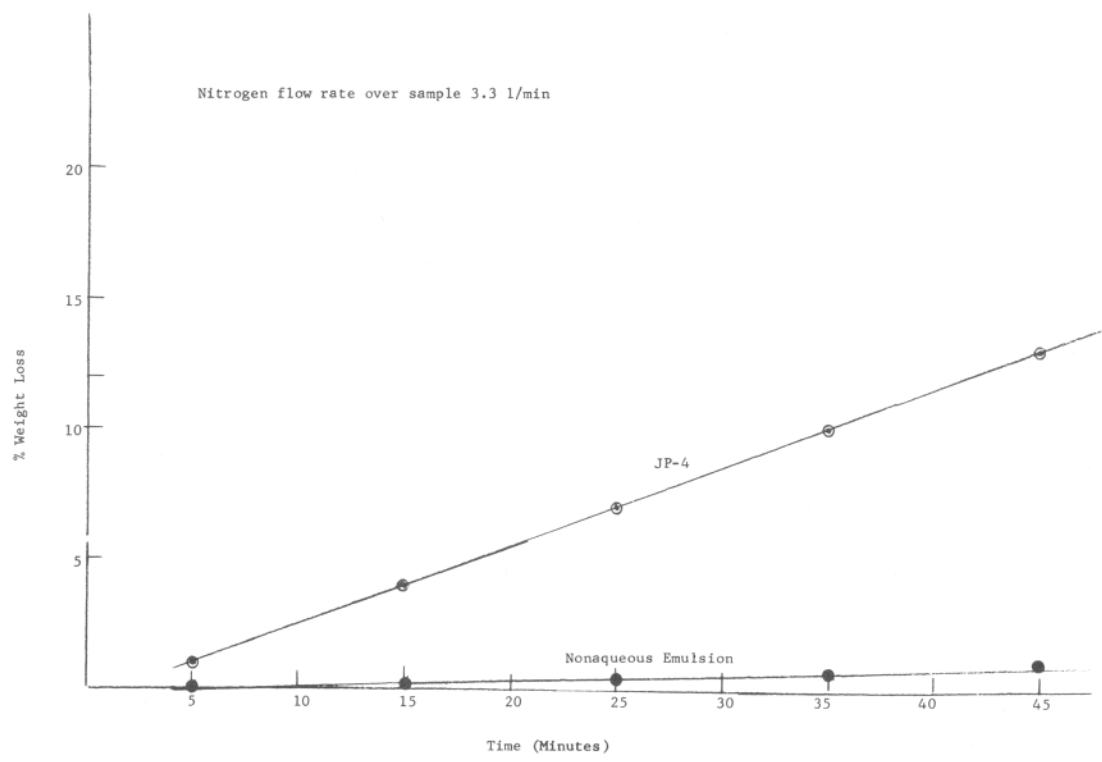


Fig. 10 - Evaporation rates for JP-4 and emulsion at -20 F

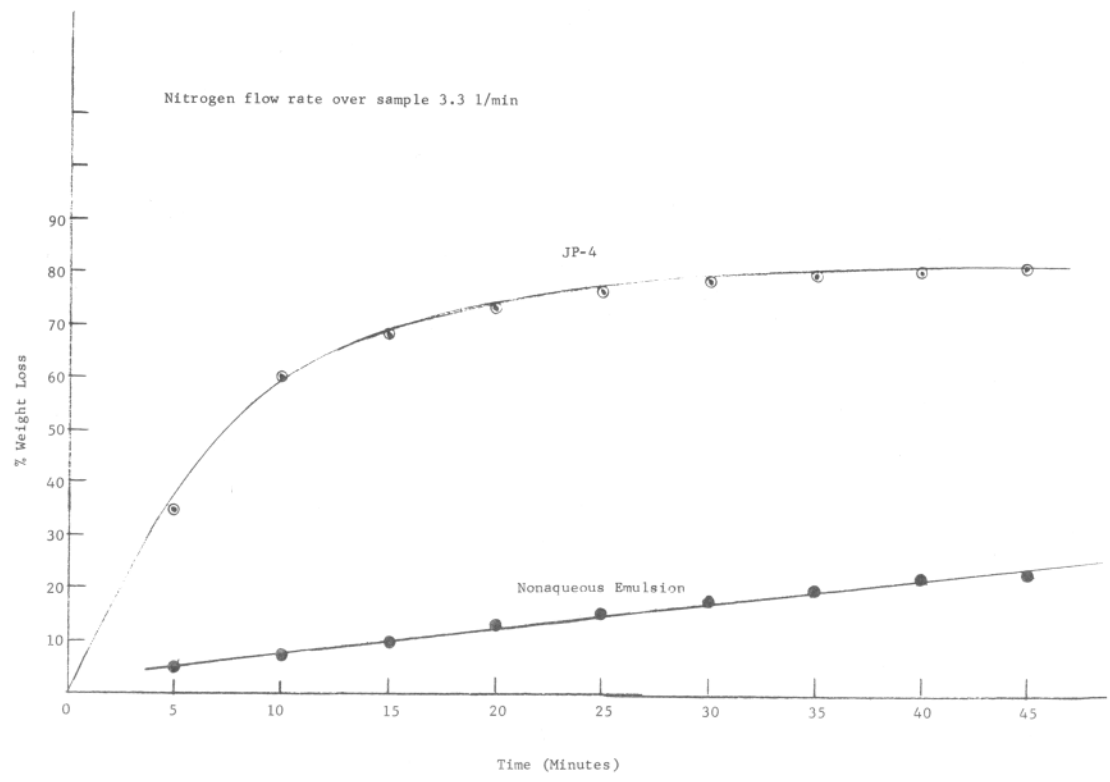


Fig. 11 - Evaporation rates for JP-4 and fuel emulsion at 25 F

indicated, both the nonaqueous and the aqueous emulsions possess yield stresses greater than that which is required to prevent atomization when a helicopter crashes at 80 mph, and the emulsion from flowing through a hole caused by a 50 caliber bullet (Fig. 8). However, the real value of these

materials must still be demonstrated under practical field conditions.

The evaporation rates of the emulsion under both static and dynamic conditions are significantly less than that of JP-4. At 130 F under static conditions emulsification reduces

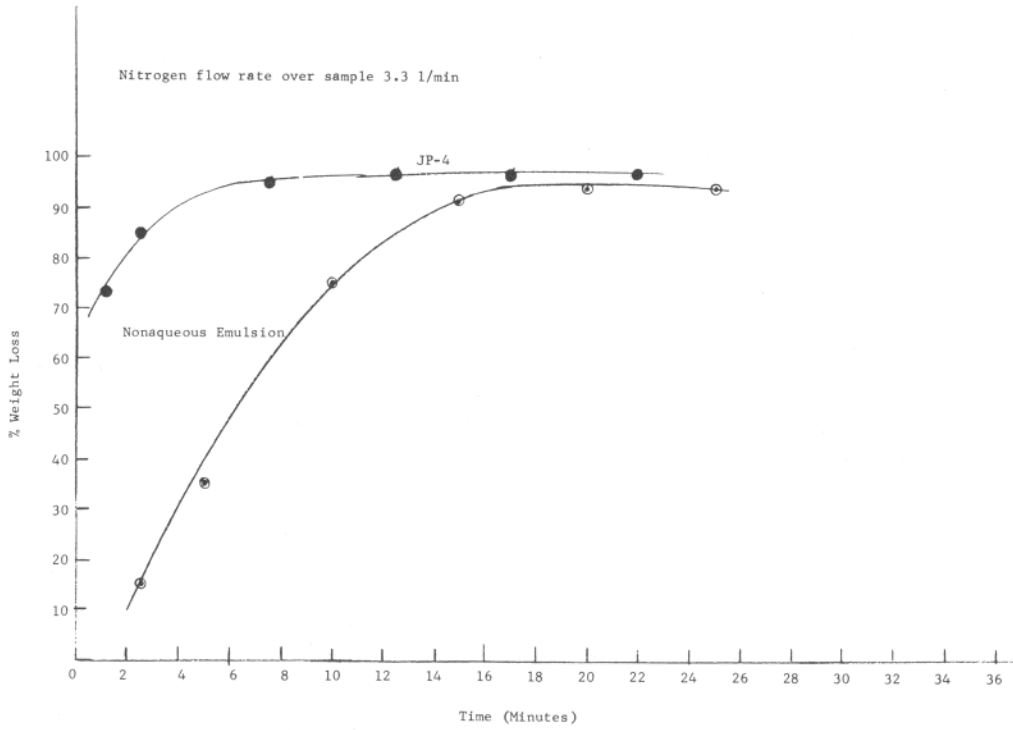


Fig. 12 - Evaporation rate of JP-4 and fuel emulsion at 130 F

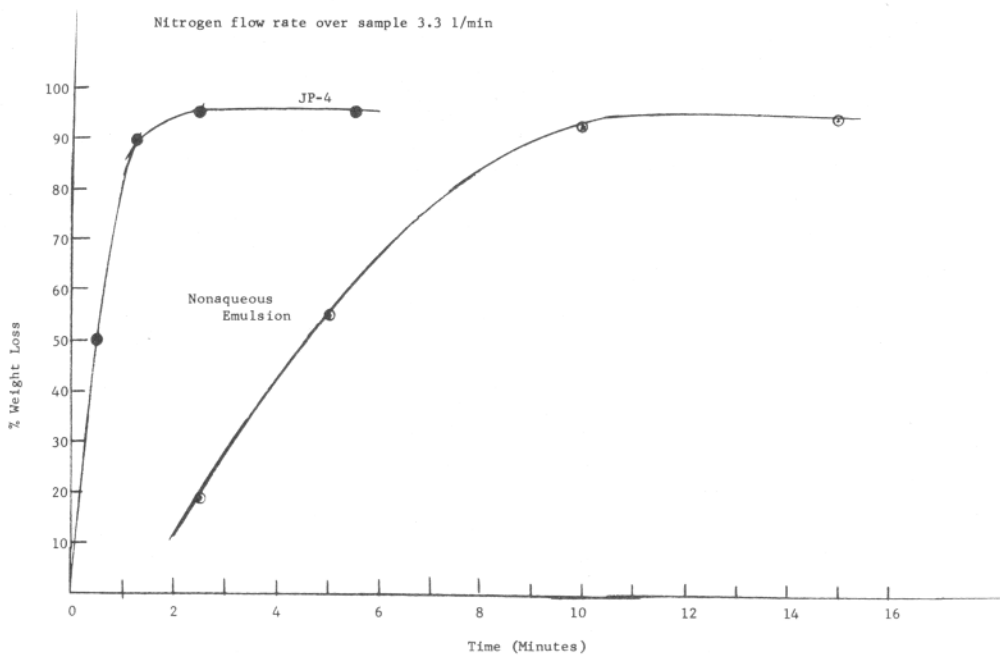


Fig. 13 - Evaporation rate of JP-4 and fuel emulsion at 160 F

the evaporation rates by 85% (Fig. 9) over that of the corresponding liquid fuel. The evaporation rates of the emulsion under dynamic conditions at all temperatures from -20 to 160 F are some 72-95% less than that of the liquid fuel (Figs. 10-13). Thus, emulsification of the fuel inhibits release of combustible vapor which, in turn, reduces the flame propagation rate of the fuel. The flame propagation rate for the emulsion is reduced by some 98% of that of the liquid fuel (see below).

	Time for Flame to Travel 2 ft, sec
JP-4	~1
JP-4 Fuel Emulsion	95

SUMMARY AND CONCLUSION

Fuel emulsions have been developed which have improved shelf life and thermal stability, and which appear to be compatible with practical materials of aircraft construction. These fuel emulsions meet most of the tentative requirements of such a fuel. The data indicate that emulsified fuels should be more advantageous than liquid fuel from the standpoint of safety. However, use of these fuels in an actual engine fuel system must be demonstrated. As engine performance data become available, it is quite likely that present formulations will have to be modified and/ or new formulations will have to be developed prior to actual helicopter flight tests. Our work at Esso is thus continuing in an effort to provide the know-how required either to modify or to develop new formulations to meet these engine requirements.



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