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FEASIBILITY STUDY OF TURBINE FUEL GELS FOR REDUCTION OF CRASH FIRE HAZARDS

FINAL REPORT

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for

FEDERAL AVIATION AGENCY
AIRCRAFT DEVELOPMENT SERVICE

SUMMARY

Several additives for gelling turbine fuel were studied and tested to predict (1) their ability to reduce or prevent fuel fire in aircraft crashes and (2) their ability to maintain the turbine engine quality of the fuel. An additive known as N-coco-γ-hydroxybutyramide (CHBA) was found to give a strong, solid gel when mixed in the ratio of 1.5 percent to the weight of the fuel. Laboratory scale impact tests in the presence of an open flame were made of several types of gels. The CHBA gave the best results and reduced the amount of flame generated by 85.2 percent as compared to ungelled fuel. Flame propagation rate on the surface of the gel was less by 96.7 percent. This gel is easily liquefied by heating it to 130^0 F.

Chemical and physical tests of the CHBA liquefied gel indicate that it meets turbine engine fuel requirements in all respects except freezing point, which is necessarily high because of the solid nature of the gel. Five gallons of liquefield CHBA gel were burned in a 0.75 gallon per hour standard commercial oil burner having a nozzle with a 60 degree cone orifice. Ignition was instantaneous and the material was visually observed to burn with a smooth, steady flame without leaving deposits or causing corrosion. In a separate test, the solid gel itself was pumped to the nozzle with a gear pump. It burned in the same manner as the liquefied gel.

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This report has been prepared by The Western Company of North America, Research Division, for the Aircraft Development Service of the Federal Aviation Agency, under Contract No. FA64WA-5053. The contents of this report reflect the views of the contractor, who is responsible for the facts and the accuracy of the data presented herein, and do not necessarily reflect the official views or policy of the FAA. This report does not consistute a standard, specification or regulation.

INTRODUCTION

Records show that the casualty rate in aircraft crashes involving fire is much greater than in those where fire does not result. Under crash conditions the fuel on board an aircraft is subject to spillage and vaporization and is therefore vulnerable to sources of ignition. These sources include hot engine components, sparks struck from metal impacts, sparks from electrical circuits, etc. The highly volatile nature of the fuel causes it to burn at a rapid rate. Under these conditions casualties from the heat and suffocation are very likely.

Several approaches have been, and are being, tried to control fuel burning in crashes. These approaches include break-away fuel tanks, elimination of ignition sources, and modification of fuel characteristics. The most promising method to date involves changing the characteristices of the fuel to reduce its vaporization and therefore its ignition susceptibility and burning rate under crash conditions. The most dramatic changes to a fuel's physical properties can be achieved by gelling it—that is, solidifying it by the addition of small amounts of gelling agents. Napalm is an example of gelled fuel. An analogy is the solidification of flavored and colored water to form Jello. Emulsifying agents also are used to drastically change the properties of liquids. Cosmetic creams and lotions contain emulsifiers. There also are agents which thicken hydrocarbon fuels to high viscosities short of gelling. Additional background information on gels is included in Appendix A.

A concept, investigation of which was started in 1963 and is still under study, is to inject gelling agents into an aircraft's fuel when a crash is imminent. Very fast gelling times available with certain gelling agents make this approach feasible. Details of these studies are contained in USATRECOM Technical Report 64-66, Contract DA44-177-TC-819 available from Defense Documentation Center, AD 613 077, and USATRECOM Technical Report 65-18 for Contract DA44-177-AMC-112(T). This work was continued as Modification 1 for Contract DA44-177-AMC-112(T). A newer concept, and the substance of this contract, is that of using a completely combustible gel which can be burned directly in a turbine engine and which provides the required hazard reduction under crash conditions.

The concept explored under this program was intended to by-pass some of the problems encountered in the rapid gel approach. The rapid gel system would involve weight penalties due to the agents carried, the injection equipment and the sensing or triggering equipment to initiate gelling. The use of pre-gelled fuel could offer benefits at all times rather than only in a known crash situation.

The work plan of this investigation consists of: (1) the screening and selection of gelling agents from a list which includes metal soaps, solvatable polymers, high molecular weight organic materials, colloids, and amine soaps; (2) the determination of properties of gelled turbine fuels prepared

from the selected agents, including temperature effects, flash point, burning rate, flame propagation rate, flow characteristics, and residue; and (3) the investigation of methods of preparing the gel for the engine including a detailed comparison of the gel so prepared with standard fuel.

This work plan was aimed at achieving the ultimate objective of the investigation, which is the selection of one or more fuel gels which can reasonably be expected to provide significant hazard reduction and operate successfully in a turbine engine. This report presents the details of the work performed, along with pertinent data, calculations, reasoning and conclusions.

DISCUSSION

Screening of Gelling Agents. More than one hundred screening tests of candidate materials have yielded data pertinent to choosing gelling agents for crash safety applications. These materials are listed in Appendix B and are referred to in the table in which they appear. Descriptions and manufacturers of each material are also given. For additive cost and weight reasons an additive concentration of 1.5 weight percent was chosen as a top limit for the screening tests. The materials screened fall into two distinct categories which require different experimental approaches, as described below.

(A) In Situ Gelling Agents. "In place" gelling occurs when certain chemical reactions are allowed to take place in the fuel. The main advantage of in situ gelling is that gelling time can be fast. Also, in some cases, the material produced by the reaction will form a gel only if it is prepared in the fuel. There are disadvantages to this method also. If gelling is very rapid the gel may be non-homogeneous due to incomplete dispersion of the agents. Two agents are required instead of one and it is also possible that the co-products of the reaction may be harmful to the gel. The rapid gelling system investigated by the Army is an in situ system. Several other in situ gelling systems were examined for use in making pre-gelled fuel for testing in the subject program.

Experimentally, three different techniques were used in preparing in situ gels. The first consisted of dissolving one of the reactants in the fuel and then adding the other reactant while stirring. This method is satisfactory for reactions which proceed slowly enough to allow the second reactant to be stirred in before the gel "sets." The second method is to dissolve one reactant in the fuel and then inject the other quickly with a hypodermic syringe. The injected stream provides the necessary mixing. The third method is the simultaneous injection of the reactants.

Previous investigation has shown that in situ gels can be formed by reacting diisocyanates with various amines in the presence of fuel. These reactions are generally rapid and gels have been prepared in one second in the laboratory. The diisocyanates and amines are organic materials and therefore completely combustible under the conditions prevailing in a turbine engine. Toluene diisocyanate has been found by other investigators to be by far the most promising of the diisocyanates. Triisocyanates are reported to be effective also. However, they are not commercially available and their laboratory preparation is exacting and not within the scope of this contract.

Toluene diisocyanate was evaluated in reactions in JP-4 with a variety of amines. Amines were chosen to react with diisocyanate because of their known usefulness in hydrocarbon systems.

(1) A wide range of primary fatty amines were evaluated. The fatty amines are prepared from naturally occurring fatty acids and therefore

are mixtures of compounds of various carbon chain lengths having an attached primary amine group. The number of carbon atoms in the chains varies from eight to eighteen. Best results were obtained with a material composed mostly of eight carbon chains and one with twelve carbon chains. Even these gels were judged to be poor in resistance to mechanical action. They broke down to an applesauce consistency upon touch. It was not possible to obtain any quantitative indication of strength. The results of these experiments are presented in Table I.

(2) Secondary and tertiary amines were tried with negative results. The fuel was not changed in appearance or viscosity by the agents. The materials and concentrations tried are given in Table II.

(3) A number of diamines were tried. The diamines also failed to show any promise. Results are shown in Table III.

(4) Secondary amines modified by the addition of from two to fifteen moles of ethylene oxide per mole of amine have been found to alter gel characteristics in other systems. They failed to produce gels when reacted with toluene diisocyanate, however. Those materials tried are listed in Table IV.

(5) Toluene diisocyanate also was reacted in the presence of JP-4 with long chain fatty alcohols to see if the alcohol group reacted in a manner similar to the amine group. These reactions caused some increase in viscosity but gels were not produced. These data are listed in Table V.

(B) Prepared Gelling Agents. The primary advantage of prepared gelling agents is that elaborate preparation and measuring apparatus are not required at the time the gel is prepared. Closer control of agent composition and purity is also possible when it is prepared separately. During the time that the <u>in situ</u> toluene diisocyanate-amine gels were being screened, new gelling additives and methods were being sought. Several experiments employing the addition of only one agent were evaluated. One of these was N-coco-γ-hydroxybutyramide (CHBA). This particular material was tried because its application to oil field gelling had shown some promise a few years ago. Good gels were made in first trials with the CHBA and this led to its detailed study and to the evaluation of many related materials.

(1) CHBA is prepared by reacting butyrolactone with coco amine at a temperature of 145° F. The product formed is one of the N-alkyl-γ hydroxybutyramides. The number of carbons in the alkyl group is usually from eight to eighteen. An experiment was made to test the gelling effects of mixing butyrolactone, fuel and coco amine, heating the mixture to 145° F and then allowing the mixture to cool. This experiment produced a good gel. The possibility of improving gel quality by substituting other primary amines for the coco amine was investigated. Several others were reacted with butyrolactone. The short chain materials, octylamine and decylamine, only thickened the fuel slightly. The others formed gels but none were better than the one made with coco amine and butyrolactone. The results of this set of experiments are given in Table VI.

(2) The gel made by heating and then cooling a mixture of butyrolactone, coco amine, and fuel was compared with the one made with

TABLE I

In Situ Gelling Tests, Diisocyanate Plus Primary Amines in JP-4

Wt. % Toluene Diisocyanate	Amine	Wt. % Amine	Wt. % Total Additives	Remarks
0.4	Armeen 18D	1.1	1.5	Increased viscosity slightly
0.4	Armeen 16D	1.1	1.5	Increased viscosity slightly
0.5	Armeen 14D	1.0	1.5	Increased viscosity slightly
0.5	Armeen 12D	1.0	1.5	Formed a weak gel
0.5	Armeen 10D	1.0	1.5	Formed a weak gel
0.5	Armeen 8D	1.0	1.5	Formed a weak gel
0.5	Armeen TD	1.0	1.5	No apparent change
0.5	Armeen HTD	1.0	1.5	No apparent change
0.5	Armeen CD	1.0	1.5	Formed a weak gel
0.48	Armeen 18D	1.19	1.67	Increased viscosity slightly
0.79	Armeen 18D	0.99	1.78	Formed slurry
0.62	Armeen 12D	1.09	1.71	Formed good gel
0.98	Armeen 12D	0.86	1.84	Very viscous solution
0.81	Armeen 8D	0.97	1.78	Formed good gel
1.20	Armeen 8D	0.72	1.92	Very viscous solution

TABLE II

In Situ Gelling Tests, Diisocyanate Plus Secondary and Tertiary Amines in JP-4

Wt. % Toluene Diisocyanate	Amine	Wt. % Amine	Wt. % Total Additives	Remarks
0.5	Armeen 2C	1.0	1.5	No apparent change
0.5	Armeen 2HT	1.0	1.5	No apparent change
0.5	Armeen 2S	1.0	1.5	No apparent change
0.5	Armeen Z	1.0	1.5	No apparent change
0.5	Armeen SZ	1.0	1.5	No apparent change
0.5	Armeen DM12D	1.0	1.5	No apparent change
0.5	Armeen DM14D	1.0	1.5	No apparent change
0.5	Armeen DM16D	1.0	1.5	No apparent change
0.5	Armeen DM18D	1.0	1.5	No apparent change
0.5	Armeen DMCD	1.0	1.5	No apparent change
0.5	Armeen DMSD	1.0	1.5	No apparent change
0.5	Armeen DMHTD	1.0	1.5	No apparent change

TABLE III

In Situ Gelling Tests, Diisocyanate Plus Diamines in JP-4

Wt. % Toluene Diisocyanate	Amine	Wt. % Amine	Wt. % Total Additive	Remarks
0.5	Duomeen C	1.0	1.5	No apparent change
0.5	Duomeen CD	1.0	1.5	No apparent change
0.5	Duomeen S	1.0	1.5	No apparent change
0.5	Duomeen T	1.0	1.5	No apparent change
0.5	Duomeen C50	1.0	1.5	No apparent change
0.5	Duomeen CD50	1.0	1.5	No apparent change
0.5	Duomeen 0	1.0	1.5	No apparent change
0.5	Oxy Bis N-N-Diethylamine	1.0	1.5	No apparent change
0.5	Duomeen TDO	1.0	1.5	No apparent change
0.5	Duomeen TMO	1.0	1.5	No apparent change
0.5	Duomeen CDA-50	1.0	1.5	No apparent change

TABLE IV

In Situ Gelling Tests, Diisocyanate Plus Polyethoxylated Amines in JP-4

Wt. % Toluene Diisocyanate	Amine	Wt. % Amine	Wt. % Total Additive	Remarks
0.5	Ethomeen C/15	1.0	1.5	Product precipitated
0.5	Ethomeen C/20	1.0	1.5	Product precipitated
0.5	Ethomeen C/25	1.0	1.5	Product precipitated
0.5	Ethomeen S/15	1.0	1.5	Product precipitated
0.5	Ethomeen T/12	1.0	1.5	Product precipitated
0.5	Ethomeen 0/15	1.0	1.5	Product precipitated

TABLE V

In Situ Gelling Tests, Diisocyanate Plus Long Chain Fatty Alcohols in JP-4

Wt. % Toluene Diisocyanate	Fatty Alcohols	Wt. % Alcohol	Wt. % Total Additive	Remarks
0.5	Dytol B-35	1.0	1.5	Increased viscosity slightly
0.5	Dytol J-68	1.0	1.5	Increased viscosity slightly
0.5	Dytol L-79	1.0	1.5	Increased viscosity slightly
0.5	Dytol L-80	1.0	1.5	Increased viscosity slightly
0.5	Dytol R-52	1.0	1.5	Increased viscosity slightly
0.5	Dytol F-11	1.0	1.5	Increased viscosity slightly
0.5	Dytol E-46	1.0	1.5	Increased viscosity slightly

TABLE VI

In Situ Gelling Tests, Butyrolactone Plus Primary Amines in JP-4

Wt. % Butyrolactone	Amine	Wt. % Amine	Wt. % Total Additives	Remarks
1.0	Armeen 8D	1.5	2.5	Slight increase in viscosity
0.9	Armeen 10D	1.6	2.5	Slight increase in viscosity
0.8	Armeen 12D(coco)	1.7	2.5	Good gel
0.7	Armeen 14D	1.8	2.5	Good gel
0.7	Armeen 16D	1.8	2.5	Good gel
0.8	Armeen HTD	1.7	2.5	Thin gel
0.8	Armeen 18D	1.7	2.5	Good gel
0.8	Armeen TD	1.7	2.5	Thin gel
0.6	Armeen SD	1.9	2.5	Slight increase in viscosity
1.0	Armeen CD	1.5	2.5	Very good gel

the pre-reacted coco amine plus butyrolactone. It was learned that a better gel is formed in the reaction product (CHBA) is dissolved in fuel at 135^0 F and then allowed to cool.

Butyrolactone was reacted with a variety of other primary fatty amines to form the solid N-alkyl-γ-hydroxybutyramides. These were dissolved in fuel at 145^0 F and allowed to cool. This method was found to give much better gels than when the same materials were mixed in the fuel and heated. The N-coco-γ-hydroxybutyramide again gave the best results. These results are tabulated and presented in Table VII.

(3) Fatty acids are the parent compounds from which the fatty amines are made. The effects of adding an excess of fatty acid to the CHBA-fuel mix were studied in a series of gelling tests. No benefits were realized from the addition of a product refined from cottonseed oil and composed mostly of oleic and lineoleic acids. Table VIII gives the results of these experiments.

(4) Success with the N-alkyl-γ-hydroxybutyramides led to the investigation of various other amides as possible gelling agents. Some of the materials gave thin gels and others only slightly thickened the fuel. The materials and results are listed in Table IX. None of these materials gave as strong gels as CHBA.

(5) Some metal soaps were dissolved in heated fuel and checked for gelling upon cooling. Very thin gels were formed by each material. These tests were not considered promising because of the thin gels formed and because the metals contained in the gel would form solid metal oxides as products of the combustion process. The addition of the solids to the hot gases would impose an additional erosion problem on the turbine engine. The metal soap experiments are presented in Table X.

(6) In addition to the fatty amines and fatty acids, several fatty alcohols were evaluated. These alcohols were dissolved in fuel at 150^0 F and then allowed to cool. The results obtained with the alcohols are recorded in Table XI and show that only very thin gels or slurries were formed.

Safety Evaluation of Selected Gels. A fuel gel will provide lessened ignitability and combustibility if it will reduce the dispersion of fuel upon impact and tank rupture. Containment of the fuel in the gel reduces vaporization and the formation of explosive mixtures. A sponge at rest holds liquids in its cells under ordinary conditions. However, if a wet sponge is subjected to impact, the cells are reduced in size in adsorbing the energy of impact and the liquid is released. Some gels are formed when fuel is entrapped in a latticework of the gelling agent. The liquid is held as in a sponge. However, an important difference is that the cell walls are more easily ruptured and the tearing apart of these walls absorbs most of the impact energy. The smaller pieces which result from this tearing apart are still gel, and the cells remaining continue to hold the liquid as before. Thus, the liquid is not available for forming a vapor cloud, and the objectives of reduced ignitability and combustibility are met.

Another type of gel is formed when the liquid molecules are forced to become oriented with respect to the molecules of the dispersed gelling agent. The impact energy in this case is absorbed by the disorienting of

TABLE VII

Gelling Tests, Products of Butyrolactone Plus Fatty Amines in JP-4

N-alkyl-γ-hydroxybutyramides	Wt. %	Remarks
N-octyl-γ-hydroxybutyramide	1.5	Slight increase in viscosity
N-decyl-γ-hydroxybutyramide	1.5	Slight increase in viscosity
N-dodecyl-γ-hydroxybutyramide	1.5	Good gel
N-tetradecyl-γ-hydroxybutyramide	1.5	Good gel
N-hexadecyl-γ-hydroxybutyramide	1.5	Good gel
N-octadecyl-γ-hydroxybutyramide	1.5	Good gel
N-heavy tallow-γ-hydroxybutyramide	1.5	Good gel
N-tallow-γ-hydroxybutyramide	1.5	Good gel
N-coco-γ-hydroxybutyramide	1.5	Very good gel

TABLE VIII

Gelling Tests, CHBA and Excess Fatty Acid in JP-4

N-Alklyamide	Wt. % Fatty Acid	Wt. % Total Additive	Remarks
1.5	0.0	1.5	Firm gel
1.3	0.2	1.5	Firm gel
1.2	0.3	1.5	Firm gel
0.9	0.6	1.5	Firm gel
0.75	0.75	1.5	Firm gel

TABLE IX

Gelling Tests, Amides in JP-4

Amide	Wt. % Amide	Remarks
Armid 8	1.5	Increased viscosity slightly
Armid HT	1.5	Increased viscosity slightly
Armid C	1.5	Increased viscosity slightly
Armid 12	1.5	Increased viscosity slightly
Armid 14	1.5	Increased viscosity slightly
Armid 16	1.5	Increased viscosity slightly
Armid 16	1.5	Increased viscosity slightly
N-tert-butylacrylamide	1.5	Thin gel formed
Cyanogum 41	1.5	Thin gel formed
Acrylamide	1.5	Thin gel formed
Polyacrylamide 50	1.5	Thin gel formed
Polyacrylamide 75	1.5	Thin gel formed
Polyacrylamide 100	1.5	Thin gel formed
Nitrilotrispropionamide	1.5	Thin gel formed

TABLE X

Gelling Tests, Metal Soaps in JP-4

Soap	Wt. % Soap	Remarks
Zinc stearate	1.5	Thin gel formed
Sodium hydroxystearate	1.5	Thin gel formed
Magnesium stearate	1.5	Thin gel formed
Aluminum octoate	1.5	Thin gel formed
Aluminum palmitate	1.5	Thin gel formed

TABLE XI

Gelling Tests, Fatty Alcohols in JP-4

Fatty Alcohols	Wt. % Alcohols	Remarks
Dytol B-35	5.0	Slightly gelled
Dytol B-35	1.5	Increased viscosity slightly
Dytol J-68	5.0	Formed a thin slurry
Dytol J-68	1.5	Increased viscosity slightly
Dytol L-79	5.0	Formed a thin gel
Dytol L-79	1.5	Thin slurry
Dytol L-80	1.5	Thin slurry
Dytol R-52	1.5	Thin slurry
Dytol F-11	1.5	Thin slurry
Dytol E-46	1.5	Thin slurry

some of the molecules. This disorientation occurs in such a manner that the gel breaks up into chunks and pieces. Orientation still prevails in these fragments and they remain as coherent masses. The fuel is, in effect, contained and not free to burn in a vapor cloud.

If ignition of the gel occurs, the speed with which the flame advances on the surface is an important indication of its safety features. If the fuel is bound to such an extent that melting of the surface from the advancing flame is required to sustain burning, then it will be difficult to ignite upon impact. Slower burning rates would also allow more time for the evacuation of a crashed aircraft.

Impact, flame propagation behavior and burning times of the gels selected in the screening tests were evaluated as described below.

(A) Impact Studies. Gels were subjected to a very severe test by hurling them through a steel grating. The object of the test was to determine the relative extent to which the gels tended to disintegrate and form an ignitable mixture upon impact.

(1) Air Gun. A compressed air gun was used to propel the 100 gram samples to the target. This gun is shown in Figure 1. The two inch diameter barrel of the air gun is five feet long. It is detachable from the breech to allow samples to be breech loaded. The breech is connected to a compressed air reservoir through a solenoid operated, quick opening, dump valve. The solenoid is activated by a signal from a high speed camera. In practice, the camera is started manually and the solenoid is activated by the camera when the selected framing rate is reached. The air gun is capable of hurling samples at speeds up to 500 feet per second (296 knots). An air pressure of 80 pounds per square inch in the reservoir will provide this speed. A standard speed of 125 miles per hour was used in evaluating the gels. The air gun proved to be a means of reliably and reproducibly obtaining the desired sample speed.

(2) Samples. Various commercial and military fuels were used in these tests. The common commercial fuel known as Jet A is very similar to the military JP-5 as both are kerosene types. JP-4 has a kerosene base with a more volatile aviation gasoline fraction. The specifications are listed in Table XII. Fuel alone was first evaluated to give a point of reference. At first, thin metal close fitting cans holding 40 milliliters were used. Upon target impact, the can was ruptured and the sample was broken up into a spray pattern behind the grating. In later tests, it was learned that thin plastic bags worked as well as the cans and allowed the use of larger samples. The inconvenience of having the cans become imbedded in the grating was also avoided.

(3) Target. A grating having one inch openings and measuring twelve by eighteen inches was used for a target. The grating effectively stopped the gel containers and broke the samples up into a spray pattern.

(4) Ignition. An acetylene torch was placed behind the target so that the sample spray passed through the flame. The flame was adjusted to a length of five-six inches to provide as much contact as possible with the spray.

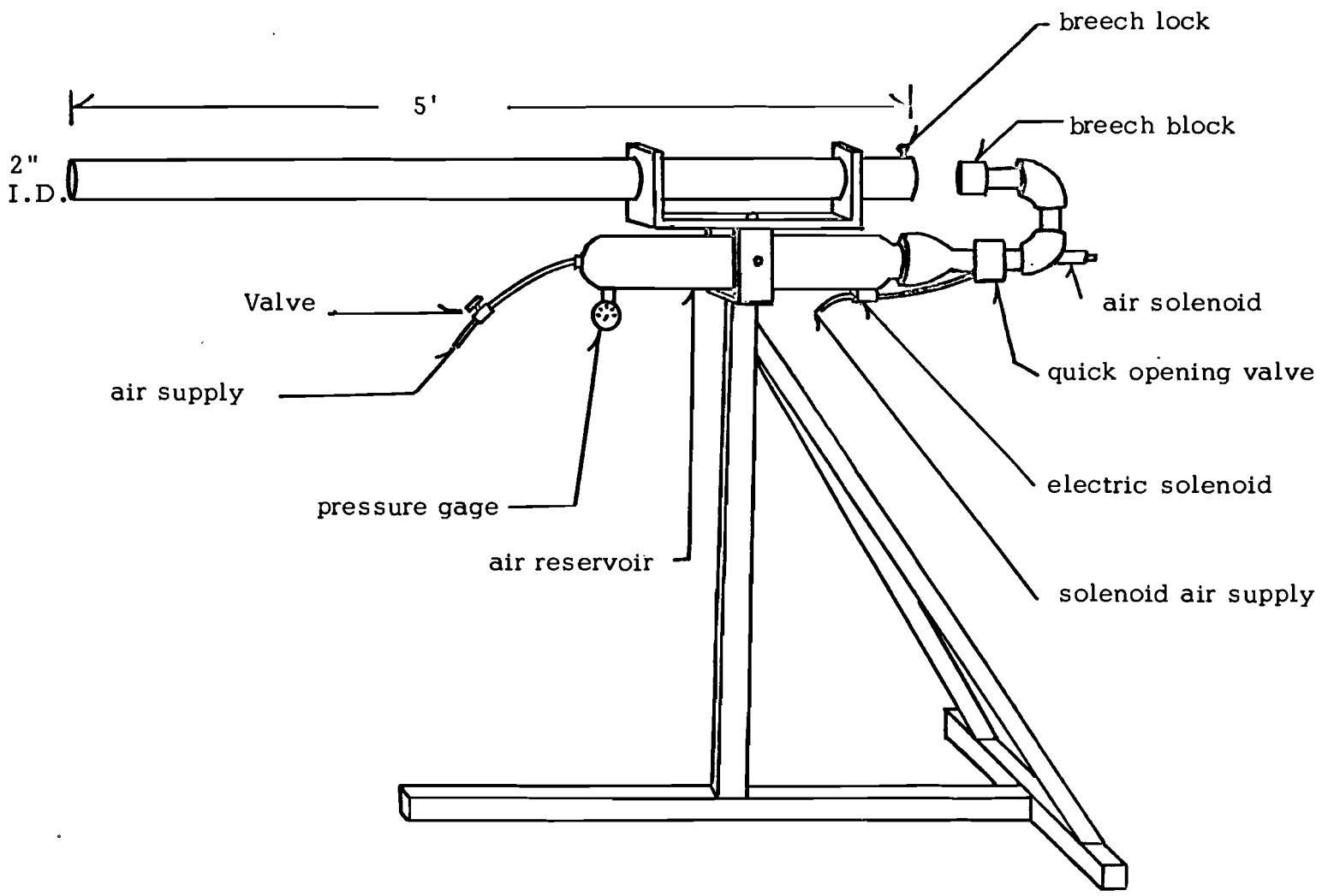

FIGURE 1

Air Gun, Breech Open

TABLE XII

Requirements, JP-4, JP-5 and Jet A Fuels

Requirements	JP-4	JP-5	Jet A
Distillation:			
Initial boiling point, min.	(1)	(1)	
Fuel evaporated, 10 percent min. at	(1)	400°F (204.4°C)	400°F (204.4°C)
Fuel evaporated, 20 percent min. at	290°F (143.4°C)	(1)	
Fuel evaporated, 50 percent min. at	370°F (187.8°C)	(1)	450°F (232.2°C)
Fuel evaporated, 90 percent min. at	470°F (243.3°C)	(1)	
End point, max.	(1)	550°F (287.8°C)	550°F (287.8°C)
Percent evaporated, at 400°F (204.4°C)	(1)		
Residue, vol. percent max.	1.5	1.5	1.5
Distillation loss, vol. percent max.	1.5	1.5	1.5
Gravity °API- min. (sp.gr.max.)	45.0 (0.802)	36.0 (0.845)	39.0 (0.823)
Gravity °API- max. (sp.gr.min.)	57.0 (0.751)	48.0 (0.788)	51.0 (0.775)
Existent gum, mg./100 ml. max.	7	7	7
Total potential residue, 16 hour aging, mg./100 ml. max.	14	14	14
Sulfur, total, percent weight max.	0.4	0.4	0.3
Mercaptan sulfur, percent weight max.	0.001	0.001	0.003
Reid vapor pressure, 100°F, psi, min., (gm./cm.^{2}, min.)	2.0 (140.6)	-	-
Reid vapor pressure, 100°F, psi, max., (gm./cm.^{2}, max.)	3.0 (210.9)	-	-
Freezing point, °F max.	-76°F (-60°C)	-55°F (-48°C)	-40°F

TABLE XII (Continued)

Requirements	JP-4	JP-5	Jet A
Heating value heat of combustion (lower or net) BTU/lb. min.	18,400	18,300	18,400
Or aniline-gravity product, min.	5,250	4,500	
Viscosity, centistokes at -30°F (-34.4°C)max.		16.5	15
Aromatics, vol. percent max.	25.0	25.0	20
Olefin. vol. percent max.	5.0	5.0	--
Smoke point, mm min.		19.0	20
Explosiveness, percent max.		50	
Flash point, min.		140°F (60.0°C)	110°F
Smoke volatility index, min.	52.0	--	--
Copper strip corrosion, ASTM classification, max.	No. 1	No. 1	No. 1
Water separometer index	(1)	(1)	± 1
Water reaction, interface rating max.	1b.	1b.	
Thermal stability:			
Change in pressure drop in 5 hours, in.Hg, max.	13	13	12
Preheater deposit	<3	<3	

(1) To be reported--not limited

(5) Motion Picture Record. A high speed camera was used to obtain motion pictures of the impact and ignition tests. The impact and ignition events occur too fast for visual observation to give good data. A framing rate of 1500 to 2000 frames per second allowed observation of the impact and ignition. The duration of the fire ball was determined by counting frames and using the appropriate timing marks which appear on the edge of the film.

(6) Discussion of the Results. When the factors of sample size, sample speed, sample container, target configuration, ignition source and ambient conditions are held constant, comparative tests of ignitability can be made with the air gun set-up described previously. The size and duration of the fire balls produced when the samples are ignited are functions of how much ignitable vapor is produced. This in turn depends upon the nature of the fuel and on how firmly the gel binds the fuel. If the fuel is effectively contained by the gel, a large percentage of the fragments will escape the ignition source. Enough vapor is almost inevitably produced to give some burning. The fact that this inevitable fire ball does not propagate and ignite the main portions of gel samples is a significant indication of the potential safety improvement provided by gelling the fuel.

The ignition of ungelled fuel was studied first. It was found that 100 milliliters of JP-4 gave a flame duration of 0.64 seconds. Examination of the film records disclosed that apparently the entire sample was consumed. This flame duration time was found to be reproducible and was taken as a standard for comparison.

The first samples compared were those gelled with toluene diisocyanate plus primary amines. The flame duration times of the best of these gels were evaluated and compared with ungelled JP-4. There was no reduction of duration time over JP-4. It is believed that diisocyanate gels at these concentrations have internal structures too fragile to withstand the magnitude of impact.

The flame duration times of CHBA gels were found to be a function of the percentage of agent used to prepare the gel. The 0.5 percent gel cut the time to less than one half that of liquid JP-4. The reduction obtained with 1.5 percent gel amounted to 85.2 percent. A graph of percent agent versus flame duration is presented in Figure 2. Results similar to these were obtained when the fuel used was Jet A.

(B) Flame Propagation Rates. A ten foot length of metal trough was used in making the flame propagation tests. The material to be tested was placed in the trough and ignited at one end. The time for the flame to reach the other end was recorded with a stop watch and on motion picture film. Ungelled JP-4 and CHBA gelled JP-4 were compared. The time recorded for the ten feet for JP-4 was 8.2 seconds, and almost 4 minutes for the 1.5 percent gel. The results of these experiments are summarized in Figure 3. It was observed that the gel melted at the surface as the flame front advanced. The melting released fuel which was then available for burning.

(C) Burning Times. Samples of ungelled fuel, toluene diisocyanate gels, and CHBA gels were burned in open top ceramic crucibles in the laboratory. Burning times for the 100 milliliter samples were essentially the

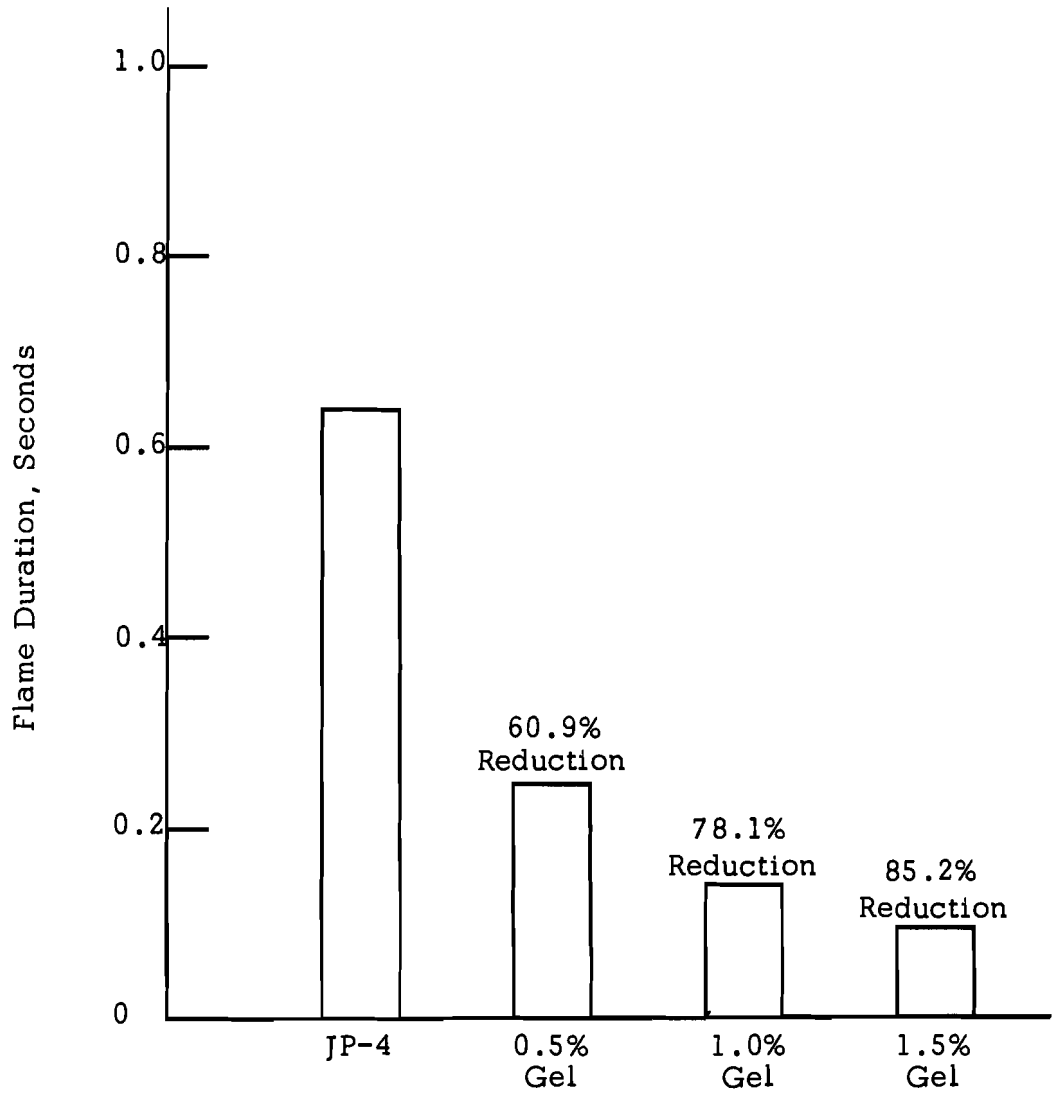

FIGURE 2

Flame Duration, Impacted CHBA JP-4 Gels

same for all materials. This arises from the fact that the gels melt at the surface and present a liquid fuel surface to the flame. The burning then occurs at a liquid surface as on ungelled fuel. This supports the conclusion that the fire hazard reduction is due both to the limiting of the dispersion and to the limiting of the exposed area. For illustration, a gallon of liquid Jet A will flow and cover many more square feet of area than a gallon of gel, even if the gel is broken up into small pieces.

Fuel Properties of CHBA Gel.

(A) Physical Properties. In order for a gelled fuel to meet the requirements for use in a turbine engine, it must have properties falling within the specifications for liquid turbine engine fuels. Some of the requirements cannot be applied to a solid gel. The freezing point of gels are necessarily high because of their solid nature. Also, the property of viscosity has no meaning for a material which does not flow in some fashion. If solid CHBA gel is subjected to the action of a viscometer, the nature of the gel is changed by the action of the viscometer. The relationship of the measured value to the original gel is undetermined. However, if the temperature of a CHBA gel is raised above its melting point, the resulting liquid can be examined and compared in all respects to liquid fuel. It is appropriate to describe separately the solid gel and the liquid obtained by liquefying the gel.

Although a single "true" viscosity cannot be assigned to the CHBA gel, an apparent viscosity can be measured under specified conditions. The CHBA gel has fluid properties under sufficient shear. The sheared gel regains its consistency slowly, but remelting is required to regain the original strength quickly. The rheological properties of CHBA gel will be discussed later.

(1) Solid Gel. The rigid gel below its melting point is an opaque, waxy solid having a slightly moist surface. It responds to stirring and handling in much the same manner as do ordinary fruit jellies. Stirring breaks it up so that is no longer "set." However, the fuel is still held in the gel structure and free liquid appears only on prolonged standing. The slightly moist surface of the gel prevents it from adhering to the walls of containers.

Two properties of the gels were routinely examined as measures of gel quality during screening and improvement experiments. These were the melting point and the penetration in ten seconds of an 89 gram, 90 degree cone. The depth of penetration of the penetrometer was recorded in millimeters. Gels which performed well in ignition and flame propagation tests were found to give penetrometer readings of 12 or less. A reading of 10 was established as a goal during gel improvement experiments. The 89 gram Westco penetrometer was used because the ASTM D217 type penetrometer is not suitable for very soft gels or those with certain rheological properties. The ASTM penetrometer can be used on the firm CHBA gel. Figure 4 gives an approximate conversion chart for the Westco and ASTM penetrometer used on the CHBA gel.

The Westco penetrometer is a penetrometer designed especially for use with soft gels and emulsions. It uses a 90 degree cone

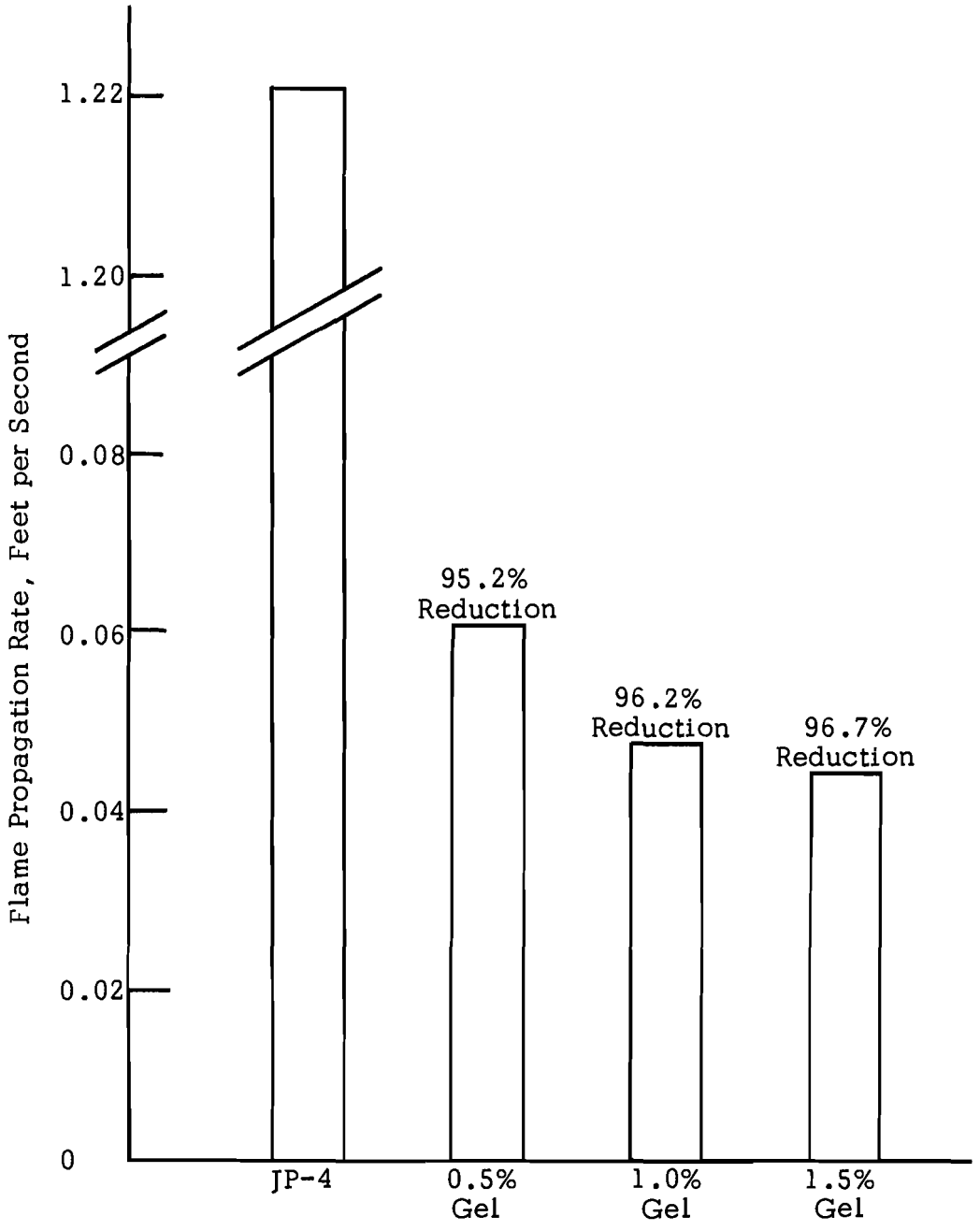

FIGURE 3

Flame Propagation Rate, CHBA JP-4 Gels

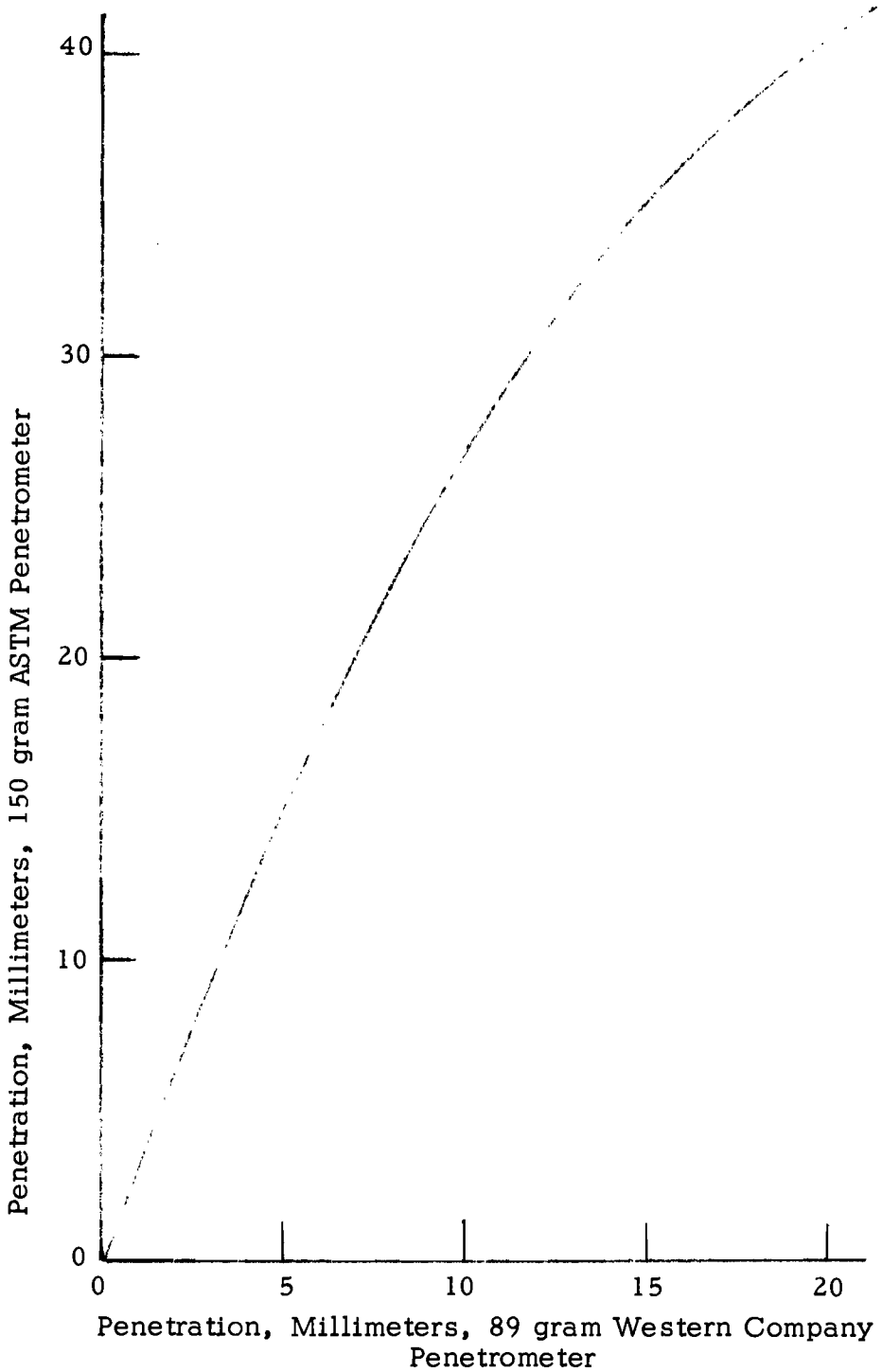

FIGURE 4
Approximate Correlation, Western Company Penetrometer vs. ASTM Penetrometer

similar to the ASTM D217 but without the ASTM needle point. The total weight applied is 89 grams versus 150 grams ASTM. The use procedures are identical.

The melting point of safety gels is important for two reasons. First, if liquefaction by melting is a part of the process of supplying gelled fuel to the engine, the size and design of the heaters will depend on the melting point. The melting point should be high enough to prevent the gel from liquefying in aircraft fuel tanks during hot weather operation. At the same time, the melting point should not be so high as to cause excessive time and power requirements in preparing the gel for the engine. Gels heated to high temperatures would also present a safety hazard.

During experimentation to improve CHBA gels, it was learned that small amounts of water in the CHBA had pronounced effects on both the melting point and strength (penetrometer reading) of the gels. It was found that increasing the water content increased the gel strength, but lowered the melting point. These findings are illustrated in Figures 5 and 6. It was learned that the pH of the CHBA and the preparation temperature of the gel also affected the strength and melting point.

Raising the pH of the CHBA from the normal 7.5-8.0 to 9.0 raised the melting point slightly. This is shown in Figure 7 which is a plot of melting point versus pH. Small amounts of hexanediamine were used to raise the pH of the CHBA. All pH adjustments were made with the CHBA molten. A pH meter was used to determine the pH. Glacial acetic acid was used for lowering the pH. The response of gel strength to changes in pH was found to be essentially nil.

The effects of gel preparation temperature on gel quality were not realized until late in the program. Some of the variations in earlier test results may have been due to lack of constant preparation temperature. The major conclusions, however, remain unchanged. The effect of preparation temperature on melting point is negligible. Gels prepared at lower temperatures have much greater strength than those prepared at higher temperatures. Figure 8 is a plot of penetration versus preparation temperature with water, pH and CHBA content held constant. For convenience, in later testing 130^0 F was established as the standard maximum temperature for preparation.

Gel strength also increases with increasing amount of agent used. Melting point varies also with percent agent but the effects are rather slight. Figure 9 shows the effects of increasing agent amount on melting point for two CHBA compositions.

Based on the experimental data discussed above, the following values were selected as the best combination to give the highest melting point consistent with adequate gel strength: N-coco-γ-hydroxybutyramide containing 6.0 percent water content, with an adjusted pH of 9.0 and 130^0 F preparation temperature of the fuel. This formulation has been designated as FAA 1069-1.

The coefficient of expansion of a 1.5 percent CHBA gel was found to be essentially that of the fuel alone. The value determined was 0.00051 gallons per gallon per degree Fahrenheit. This compares to 0.00050 gallons per gallon per degree for Jet A fuel alone.

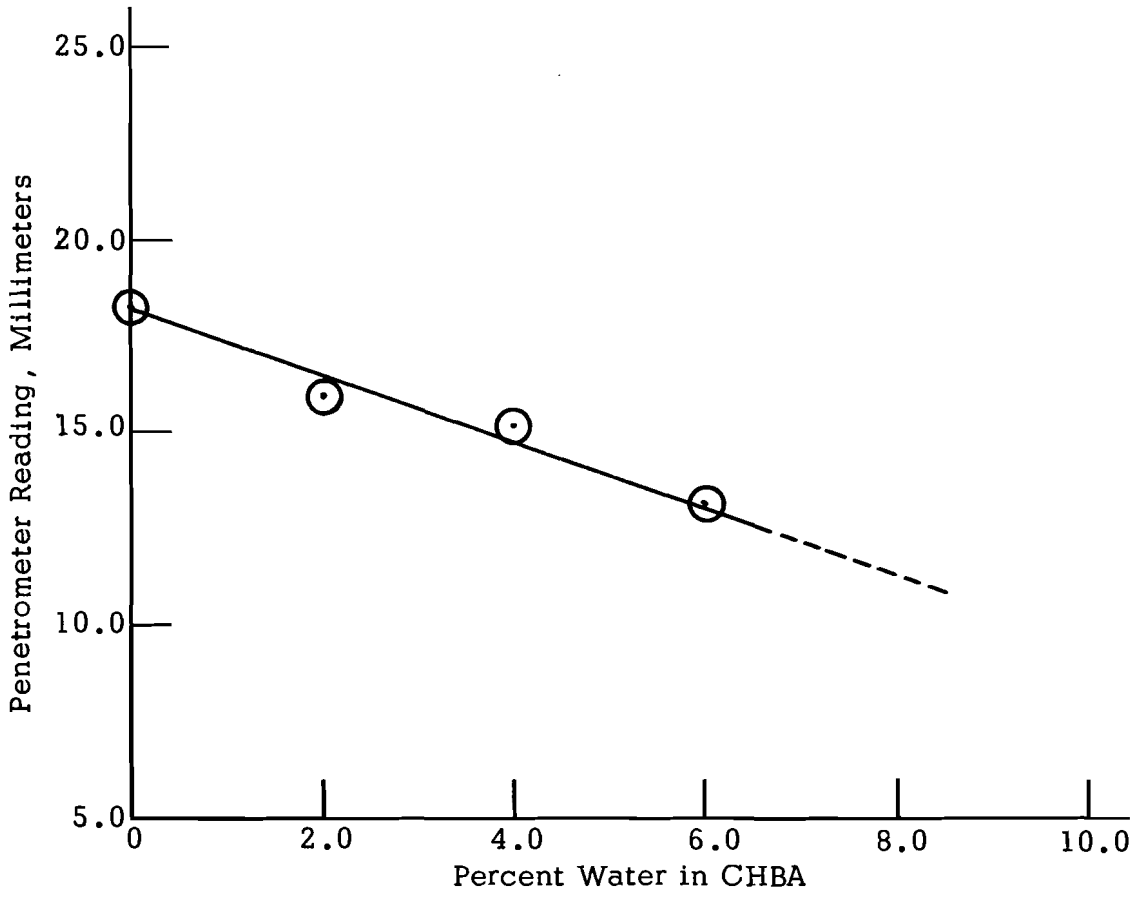

FIGURE 5

Effects of CHBA Water Content on Strength of JP-4 Gels

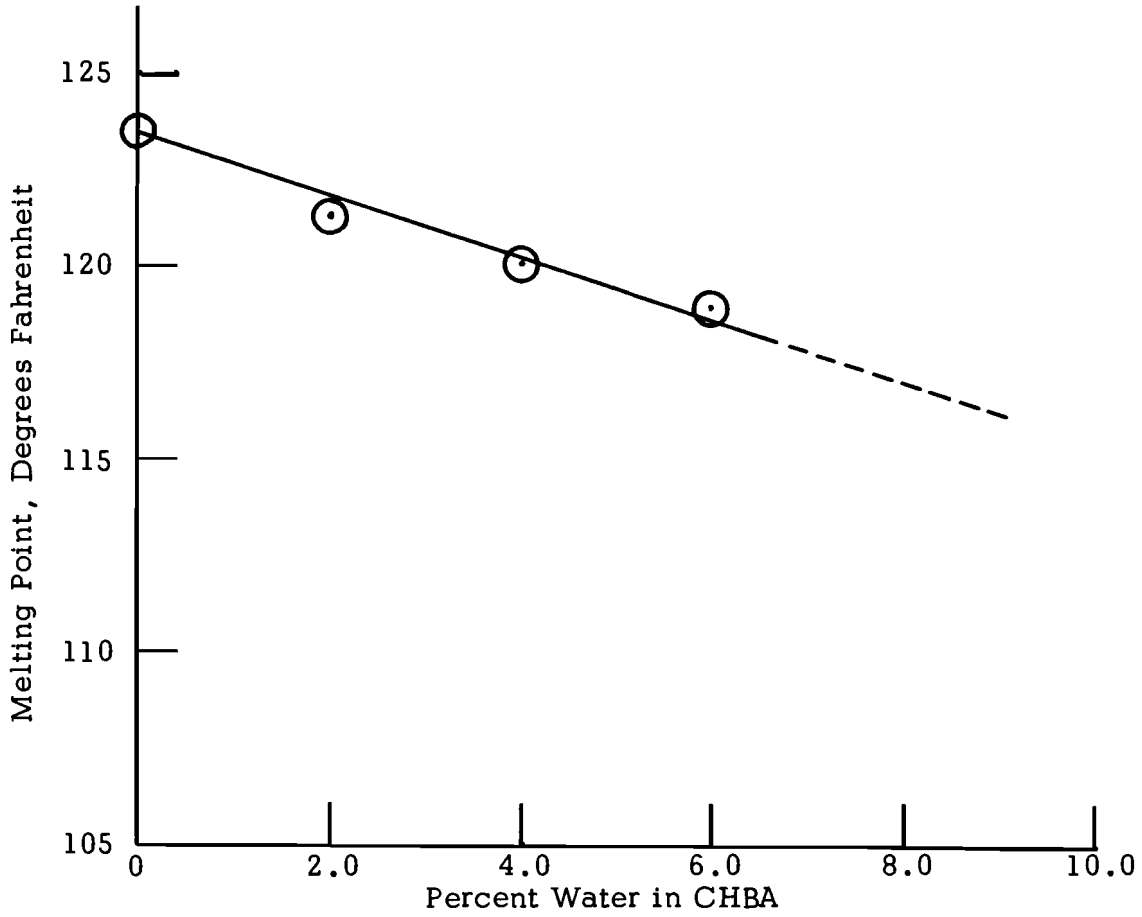

FIGURE 6

Effects of CHBA Water Content on Melting Point of JP-4 Gels

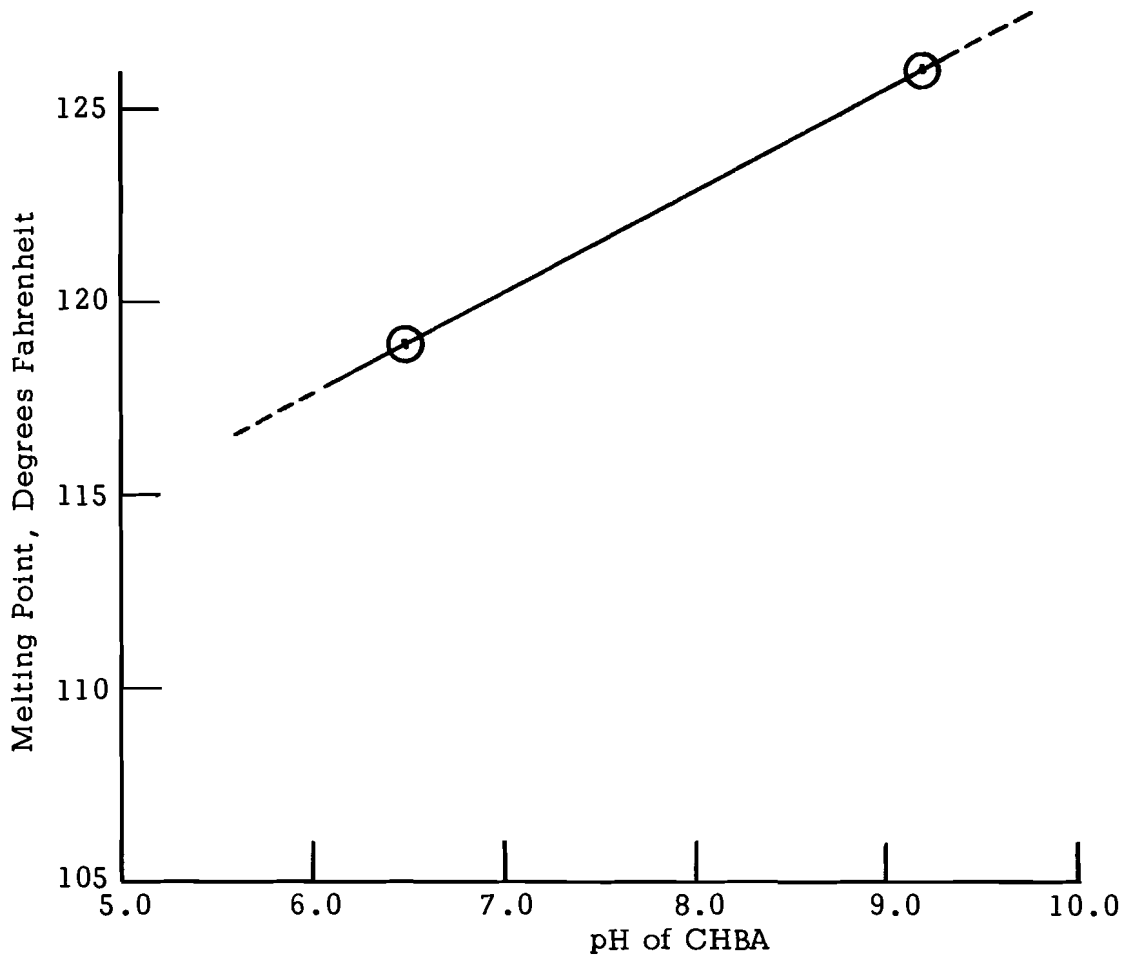

FIGURE 7

Effects of CHBA pH on JP-4 Gel Melting Point

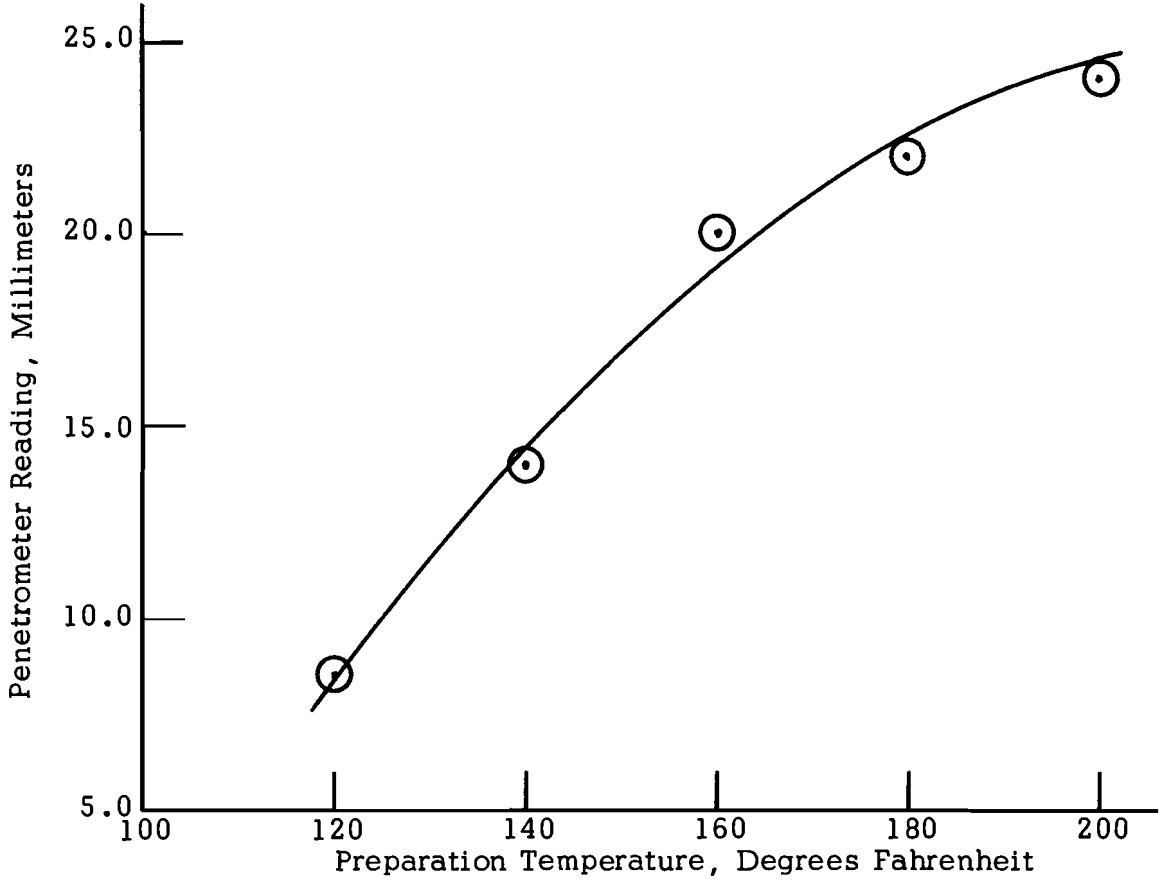

FIGURE 8

Variation of JP-4 Gel Strength with Preparation Temperature

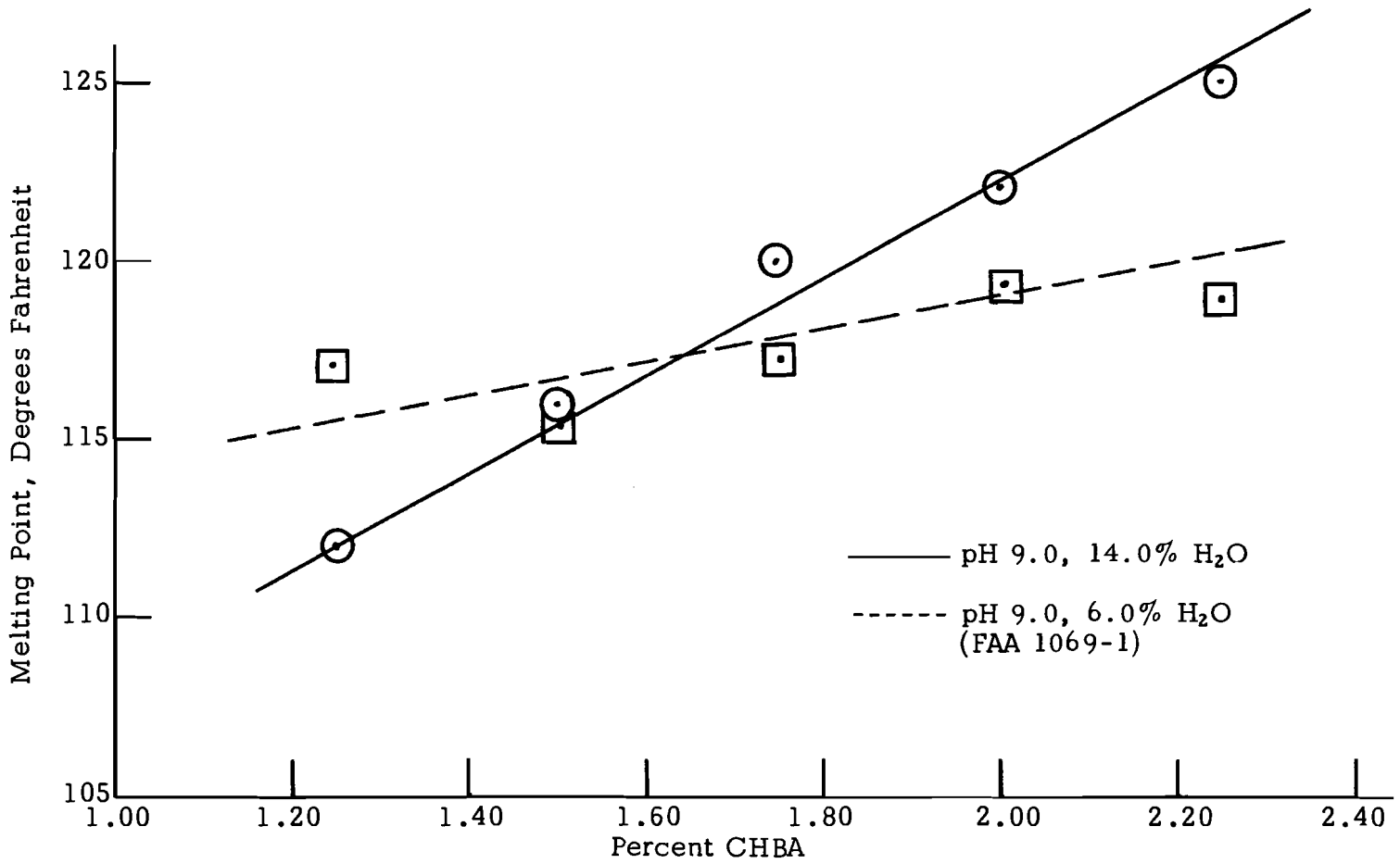

FIGURE 9

Variation of Gel Melting Point with % CHBA

The flash point of CHBA gels was determined to be that of the fuel from which it was prepared. Flash points are determined under static conditions. Flash points, like static burning times, cannot be directly used to anticipate dynamic behavior. Gels restrict the rate at which fuel becomes available for forming combustible vapor.

Fuel contained in a gel continues to exert a vapor pressure. At equilibrium the vapor pressure of a gel is the same as that of the fuel from which it is prepared. Here again, however, the dynamic behavior is different from the static behavior. If a gel at equilibrium with its vapor pressure is raised to a higher temperature it will come to equilibrium at a different pressure at the new temperature. The new pressure will be the same as that obtained with fuel alone but the time required to reach equilibrium is much longer. Figure 10 shows a comparison of the vapor pressure rise with time of gelled and ungelled fuel.

To test for inorganic, non-combustible substances in the CHBA gels, an ignited residue test was made and compared with the same test of the fuel alone. The samples were evaporated to dryness and the residue was subjected to a temperature of 1470° F for twelve hours. Within experimental error, the ignited residue found was 0.010 percent for both fuel and gel. This means that gelling a fuel with CHBA does not add any additional material which would survive the combustion temperature in a turbine engine.

(2) Liquefied Gel. CHBA gels can be most conveniently brought to the liquid state by raising their temperature to their melting point. The gels melt at low enough temperatures that the liquid can be subjected to the usual analytical tests for liquids. This allows direct comparison of the liquefied gel properties with those of the ungelled fuel. The services of a qualified testing laboratory were used to make a direct comparison of physical and chemical properties of fuel and gel. ASTM standard methods were followed. The comparison shows that the two are essentially the same except for the wide difference in melting points. The distillation residue from the gelled fuel is higher than from the fuel, but remains within the specification limit for Jet A fuel. The results obtained by the testing laboratory are given in Table XIII. The CHBA gels have withstood many rigorous comparative and independent tests. The possibility that some untested factor would cause difficulty in a turbine engine is considered to be very unlikely.

(B) Engineering Properties. The physical properties of a liquefied CHBA gel indicate that it can be handled with the usual hydraulic equipment. Further tests were made to evaluate both the gel and liquefied gel in approximately simulated actual use. These tests were designed to reveal further details concerning the pumping and burning characteristics of the material.

(1) Solid Gel. A 0.75 gallon per hour oil burner was used to burn and compare Jet A fuel and gelled Jet A fuel. The nozzle contained an orifice designed to give a 60 degree spray cone.

In the first experiments, the gel was liquefied by heating before it was fed to the pump. This liquefied gel pumped and burned in a smooth, even manner indistinguishable from that of the ungelled fuel. In later experiments, it was learned that the gear pump would pull the solid gel from the bottom of a funnel and pump it through the nozzle. The spray pattern was the same

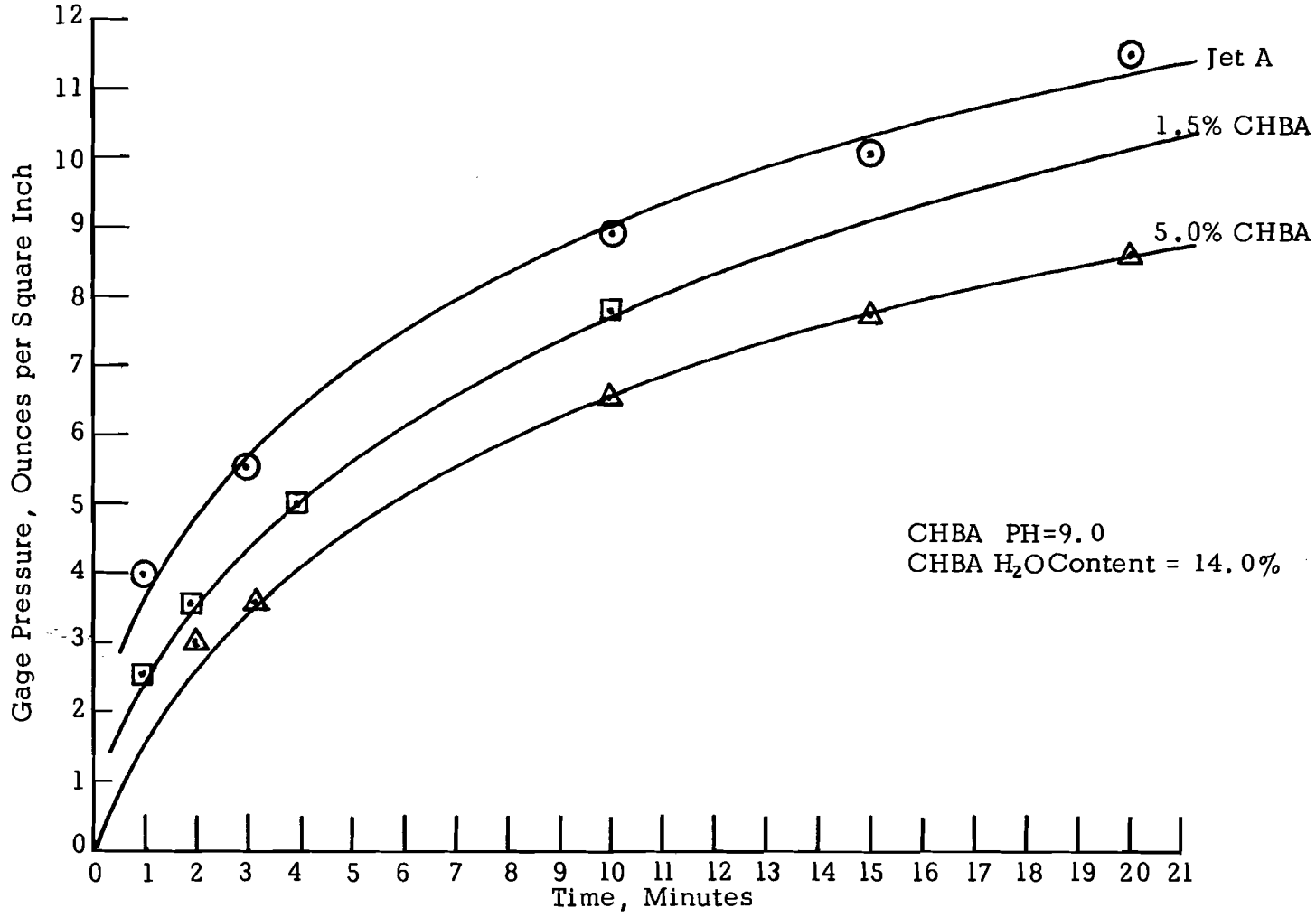

FIGURE 10

Vapor Pressure vs Time, Jet A Fuel and Jet A Gels

TABLE XIII

Comparison of Characteristics, Jet A Fuel and Gelled Jet A Fuel

Characteristic	Jet A Fuel	Gelled Jet A Fuel
API Gravity @ 60°F	42.8	43.0
Specific Gravity	0.8123	0.8109
Pounds per Gallon	6.763	6.752
Aniline No.	63.0°C	62.2°C
Flash Point (Closed Cup)	132°F	133°F
Total sulfur	None	None
Viscosity @ 100°F, SSU	32.2	--
Viscosity @ 122°F, SSU	31.9	31.4
Acidity	0.036%	0.060%
Copper strip corrosion	Class I	Class I
Freezing point	-72°F	115°F
Heat of Combustion	19,679 BTU/lb.	19,518 BTU/lb.
Distillation		
IBP	338°F	330°F
10%	370	370
20%	380	380
30%	388	390
40%	396	398
50%	406	408
60%	418	420
70%	430	434
80%	446	450
90%	466	470
EP	510	528
Residue	0.8%	1.5%
Total Recovery	100.0%	100.0%
Loss	None	None

as before. Good, positive, instantaneous ignition was obtained at all times. The ignition source was the regular electric arc starter.

A five gallon drum was fitted with a 1/2 inch draw off connection in the bottom and tried in place of the funnel. It was found necessary to provide the can with a close fitting follower plate in order to keep gel supplied to the pump. Using the follower plate arrangement, five gallons of gel were burned in the heater. Pumping and burning were completely satisfactory. The chief function of the follower plate was to prevent air channeling through the gel. Properly prepared gel required only atmospheric pressure on the follower. Very strong gels required 0-5 psig.

The foregoing experiments indicate that (as would be expected) the configuration of the container affects the ease of withdrawal of gelled fuel. The withdrawal technique must take container configuration into account.

Copper test strips were placed in the burning zone one inch from the mixing zone to check for burner deposits. Both the fuel and the gel were found to impart a slight gray appearance to the copper coupons. After the tests, the burner was disassembled and examined. The examination disclosed no unusual effect to the nozzle, orifice, or combustion chamber.

Copper and mild steel test coupons have shown no corrosion after being immersed in regular CHBA gel for six months. Copper test pieces stored in a gel made with an acidic CHBA became coated with a blue film after three weeks. The CHBA pH had been adjusted to 5.0 with acetic acid. Coupons in gels prepared from 6.0 pH CHBA (also adjusted with acetic acid) were not attacked. For this reason, as well as other reasons already presented, the neutral or basic CHBA are more suitable for turbine fuel gelling.

Separate CHBA gel samples have been stored at room temperature and at -50^0 F and have been found to be stable and free of fuel bleeding at these temperatures. The penetrometer readings of a sample prepared with FAA 1069-1 were compared at 72, 20 and -17^0 F. The readings were 17.5, 17.0 and 14.5 respectively. The response of the sample to probing at -17^0 F showed essentially no change by visual observation. The behavior of the gel at high temperatures parallels that of the ungelled fuel. This is shown by the distillation results presented in Table XIII.

Preliminary rheological testing was done on the CHBA gel, formulation FAA 1069-1, in order to estimate the pumping behavior. The results indicate that the gel approximates a Bingham Body material. That is to say that the gel has a finite yield stress, but shear thins beyond its yield stress. The initial yield stress appears to be responsible for the impact resisting properties desirable for crash protection. The fluidity beyond the yield stress gives ease of pumping and explains the success in pumping the gel in the oil burner tests. Figure 11 shows a plot of shear stress versus shear rate. The approximate yield stress is usually obtained by extrapolating the line to zero shear rate. A direct measurement of the yield stress of material of this type is difficult. These data were obtained with a Ruska constant shear rate apparatus.

(2) Liquefied Gel. Comparison of the physical properties of liquefied gel with those of the ungelled fuel leads to the belief that the engineering behavior of the two are the same. Two of the important engi-

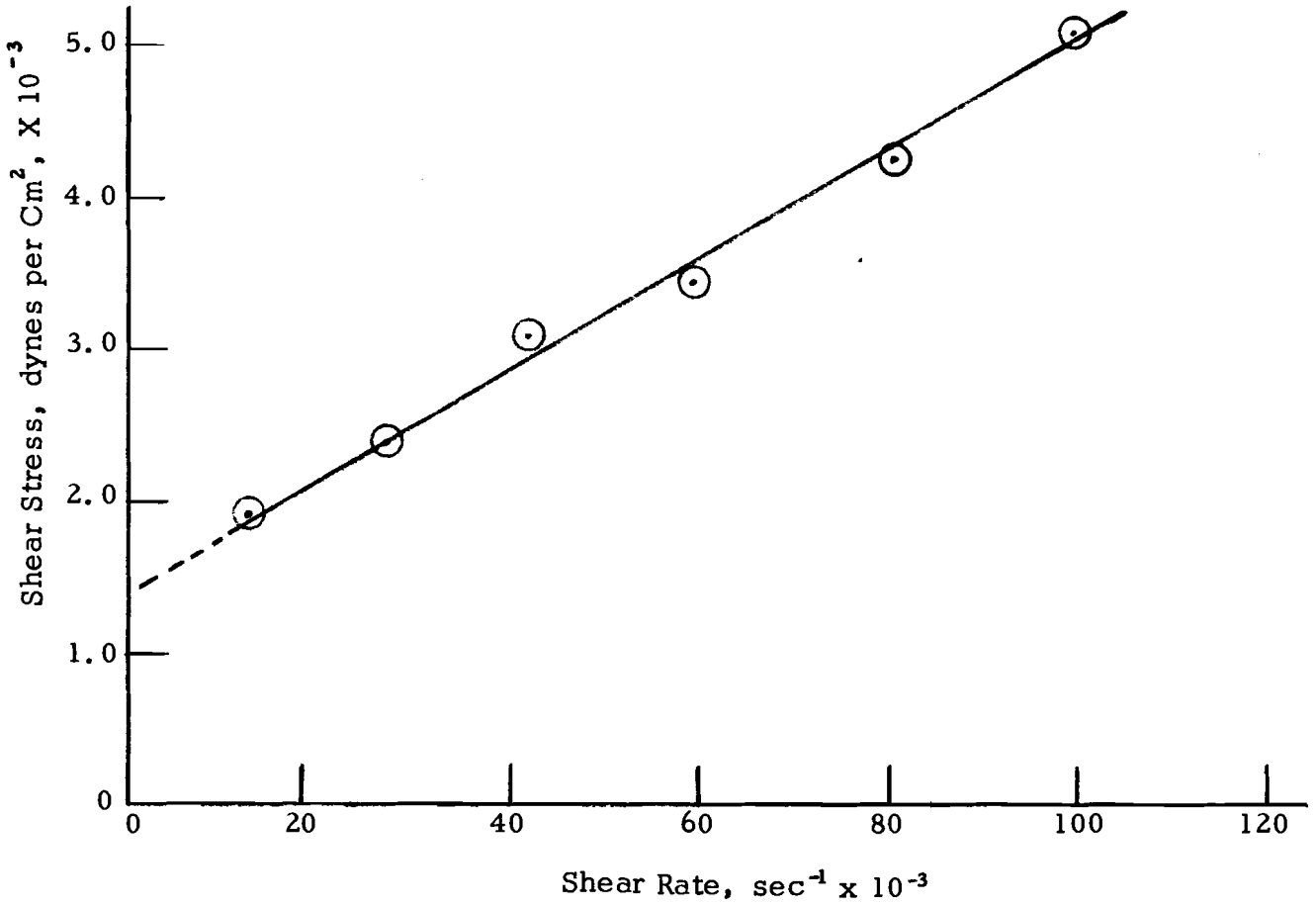

FIGURE 11
Experimental Stress-Strain Curve,
CHBA gel, FAA 1069-1

neering operations performed on fuels in an aircraft are pumping and filtering. Pumping properties of the liquefied gel were tested in connection with the burner tests and found to be completely satisfactory. A test of its filtering behavior was made with an in-line 75 micron, 14 square inch micropore woven screen filter. At 1.82 gallons per minute flow rate, the temperature was varied from 130^0 F to 140^0 F and the gauge pressure on the downstream side of the filter was varied between 8 and 25 psig. The maximum pressure drop across the filter was 1.0 psi and was identical to that found with ungelled fuel under the same conditions.

CONCLUSIONS

This investigation has provided information on the control of flamability of aircraft fuel which substantiates the following conclusions:

(A) Aircraft fuel gelled with CHBA (N-coco-γ-hydroxybutyramide) has greatly reduced ignitability and combustibility under small scale simulated crash conditions and the gelled fuel is apparently of turbine engine quality.

(B) The fire reduction benefits of gels result from their ability to physically bind the fuel and drastically restrict its freedom to vaporize, and at the same time hold to a minimum the exposed surface area available to support a fire.

(C) The CHBA gels, which are solid gels, are much more effective in reducing ignitability and combustibility than thickened fuel or "soupy" gels. The solid gel reduced flame duration of impact flash fires by 85 percent. None of the thickened fluid gels approached this performance.

(D) A very effective, strong, stable, non-corrosive, solid gel can be made by heating to 130^0 F and then cooling, aircraft fuel which contains 1.5 weight percent CHBA.

(E) Solid CHBA gels can be pumped from the bottom of a container if slight pressure is applied to the top of the gel. These gels can be pumped with gear and piston pumps of conventional design.

(F) Pressurization, or some other technique, is required to keep a gel supplied to the pump when gel is pumped from a container.

(G) CHBA gels can be liquefied by heating to 130^0 F, and the liquid obtained meets Mil Spec No. 5624F in all respects except freezing point.

(H) CHBA gels are ignitable with a standard igniter in a standard oil burner and burn with a smooth, even flame without leaving a deposit or causing corrosion.

(I) CHBA gels melt at $120\text{-}125^0$ F. More information is needed on the temperatures expected in aircraft fuel cells and the melting point most desirable for crash safety applications.

(J) The strength and melting point of CHBA gels can be modified by including small amounts of water in the CHBA, by changing its pH, and by altering gel preparation techniques. The full potential available from these and other changes has not been realized.

(K) CHBA burns without leaving a residue.

APPENDIX A

DISCUSSION OF GEL FUNDAMENTALS

APPENDIX A

A gel is a liquid with modified fluid properties. Gelling agents are materials which exhibit the ability to change the fluid properties of liquids. In general, gels consist of normally solid materials dispersed in a liquid. Gels are closely related to and share some properties of emulsions, which are dispersions of liquids in liquids. Not all colloidal dispersions of solids in liquids are gels. Many solid-in-liquid dispersions form what are called "sols," such as clay or fine metallic particles in water. The gels and emulsions are readily distinguished from the sols, which are also dispersions of solids in liquids.

Sols are very sensitive to the presence of polyvalent ions and changes in pH. The solid particles dispersed in sols are kept in suspension by Brownian Motion, the random motion of small particles and molecules. There is little interaction between the particles of solids in a sol, or between solid and liquid molecules; thus the viscosity and fluid properties of the liquid are virtually unaffected.

Gels and emulsions are affected by pH and ions in a solution, but to a much smaller degree than are the sols. In gels and emulsions, there are strong interactions with liquid molecules, or so-called solvent effects. Due to these interactions, the fluid properties such as viscosity may be greatly affected. In fact, the interactions are frequently strong enough that the gel or emulsions may resemble a solid more than a liquid in gross properties. The ordinary concept of viscosity may be inapplicable. Gels may exhibit a finite (even large) yield strength or a Young's Modulus. The physical properties of gels may be rate dependent, so that non-linear stress-strain rate and stress relaxation properties are observed. Gels are classified according to these properties. Some gels show a finite yield strength and can retain a limited amount of residual shear stress. Above their yield stress, these gels exhibit plastic flow. Thixotropic gels are those which thin or appear to lose viscosity with time under shear. Rheopectic gels appear to gain viscosity or thicken with time under shear conditions. Dilatant gels exhibit thickening or apparent increase in viscosity with increasing shear rate. Dilatant and pseudoplastic gels may also have time dependent properties superimposed. This means that a certain period of time is required for the gel to regain its initial properties after removal of an applied stress. The rheological properties of gels (thixotropy, rheopexy, dilatancy and pseudoplasticity) are generally affected by temperature. A gel may exhibit more than one of these properties over different ranges of temperature, stress and shear rate.

There is another type of material known as a Bingham Body. This material has a finite yield stress, but exhibits shear thinning rather than plastic flow when sheared beyond the yield stress. True Bingham Bodies are rare, but certain lubricating greases behave in this fashion.

The rheological and other physical properties of gels are important in considering them for use in fuel safety applications. Under the conditions of stress the fuel encounters in an aircraft crash, the gel must resist breaking up into tiny droplets and resist liquefying and wetting the surrounding area. A gel which can do this should greatly reduce the intensity and extent of any fire around the aircraft. It has been found that gels and partially gelled fuels which do not resist atomization provide little protection. To reduce the fire hazard, the rheological properties must be such that atomization does not occur under the shear experienced in a crash.

The chemical aspects of the formation and properties of gels are part of the field of surface chemistry. Gels are common in everyday experience, but not obvious. Most adhesives, for example, are gels. Many glues are gels formed from animal or vegetable proteins. These gels may be observed on the surface of cooked meat after cooling. Vegetable gels are widely used as thickening agents in food products. These protein gels have been used as adhesives and food thickeners for over 5,000 years. The use of gels to thicken materials other than foods and water has greatly increased in the last 100 years. Cosmetics and lubricants are commonly gelled non-aqueous materials.

From a chemical viewpoint, the chief aspect of gel or emulsion formation is interfacial tension. There is a layer of more or less bound material at the interface of solid wetted by liquid, or between immiscible liquids. The action of certain materials in promoting formation of gels and emulsions has been shown experimentally to be due to interface effects. A material which lowers interfacial tension concentrates in the interface and makes it more stable. Such a material may be a third component in the case of agents for emulsifying two liquids or wetting agents for solids, or the material may be a part of the solid component itself in the case of gelling materials.

Interfacial action of materials may be explained thermodynamically. A reaction is found to be spontaneous if it results in a lowering of the free energy of the thermodynamic system. Lowering interfacial tension lowers the free energy of an interface. As a result, materials in solution which can lower interfacial tension tend to concentrate in the interface. The interface then becomes a film which may be weak (called gaseous form film) or strong (called condensed film in analogy to a liquid). Material such as soaps of fatty organic molecules possess these properties in water-oil systems. The fatty chain of the soap locates in the hydrocarbon side of the interface while the cationic end (such as $-COONa$, $-SO_3Na$ or $-NH_2$) locates in the water side. Double bonds in the fatty chain tend to make the soap molecule lay over from the position which saturated molecules assume (normal to interface). Figure 12 shows soap molecules in an oil-water interface.

Solid materials such as clay particles can stabilize liquid interfaces because they absorb ions on the particle faces and lower the free energy of the interface. Due to the fact that most materials which have interfacial activity produce an electric field when oriented in an interface, the system is somewhat sensitive to pH, ionic effects and electric fields. The charged surface active materials move under the influence of electric fields unless they are neutralized by ions in solution. When the neutralization is expressed in terms of a solution pH, this pH is called the isoelectric point.

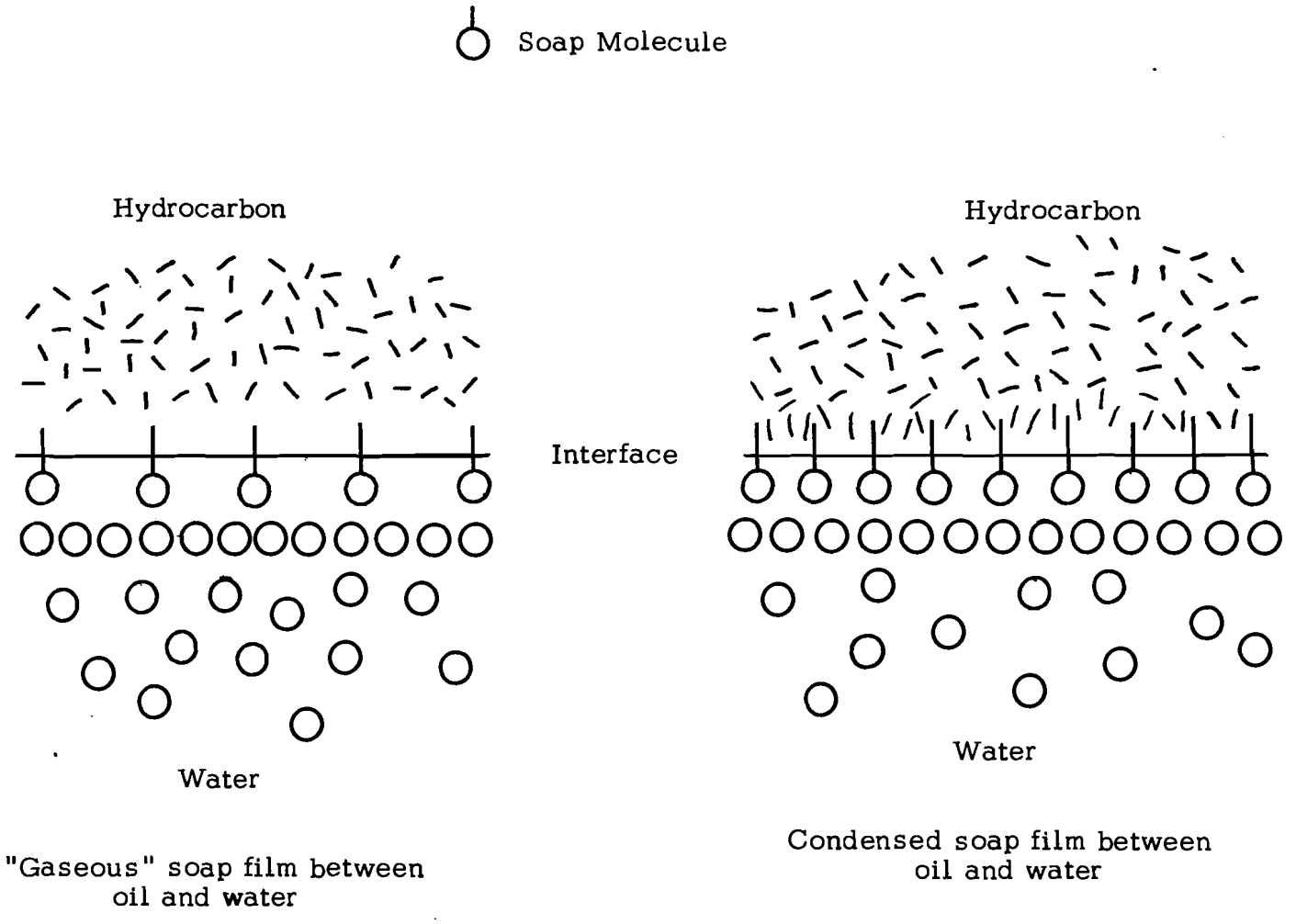

FIGURE 12

Orientation of Soap Molecules in an Oil-Water Interface

At the isoelectric point, the solution ions have maximum effect on the surface active materials. As a result, gels and emulsions are weakest and least stable at their isoelectric point.

Gels may be formed in several ways and can be classified accordingly. Cooling gelling is a common phenomenon, found in the gelling of water by some proteins (such as gelatine) or starches. The solubility of many materials increases with temperature. Lowering the temperature of a partially solublized protein in water lowers the solublization so that a gel is formed by protein particles surrounded by a solvates sheath. The protein particles form a lattice-like structure which entraps the liquid in a manner analogous to a sponge. The alkyl hydroxyamides investigated under this contract fall into the class of cooling gels. The solid material has limited solubility in fuel, but the melted amide is miscible with fuel. Thus, a gel is formed by cooling a mixture of fuel and melted amide. As the freezing point of the amide in solution is reached, particles of solid surrounded by solvated sheaths are formed. Figure 13 illustrates this. This gelling process can be reversed or repeated.

Heat gelling materials form gels by aggregation or coagulation of materials in solution. Boiling eggs or milk are familiar examples. The hardening of a boiled egg is due to coagulation of proteins to form a gel. Examples of this process in hydrocarbons are not known.

Chemical gelling can take place when a material in solution undergoes a chemical reaction which reduces its solubility. These reactions may be polymerizations, condensations or simple ionic reactions. The criterion for gel formation is that the product must be soluble enough to prevent precipitation, but not completely soluble. This balance may be very delicate. Examples of these systems which gel hydrocarbons are: in situ saponification of fatty acids or reaction of lactones with fatty amides; reaction of amines and isocyanates in fuels; and polymerization of styrene in mixtures of aromatic and aliphatic hydrocarbons. Chemical gelling is unique in that it modifies the properties of material in solution.

Forming a gel by solvent effects is the opposite of chemical gelling. Solvent effect gelling involves modifying the solvent properties of a solution so that a material dissolved in it becomes less soluble. If the proper balance between solubility and insolubility is found, a gel can be formed. An example of this process in hydrocarbons is found in the production of rubber cement. Dissolving certain polymers in gasoline or benzene gives a very viscous material. Adding a small amount of non-solvent (for the polymer) such as alcohol can convert the solution to a gel. The amount of alcohol added varies the physical nature of the gel.

Gelling may also result from the addition of very fine particles to liquids if the particles have high surface area and are wet by the liquids. Examples of this are the thickening of liquids with carbon blacks, silica gel or clays such as bentonite. The adsorption may be non-specific such as the thickening of hydrocarbons and non-polar solvents with carbon; or adsorption may be specific where certain species are preferentially adsorbed on particle surfaces. Non-polar materials tend to absorb on non-polar surfaces, such as hydrocarbons on carbon, while polar liquids prefer polar surfaces. Polar surfaces may be due to surface structures or ions

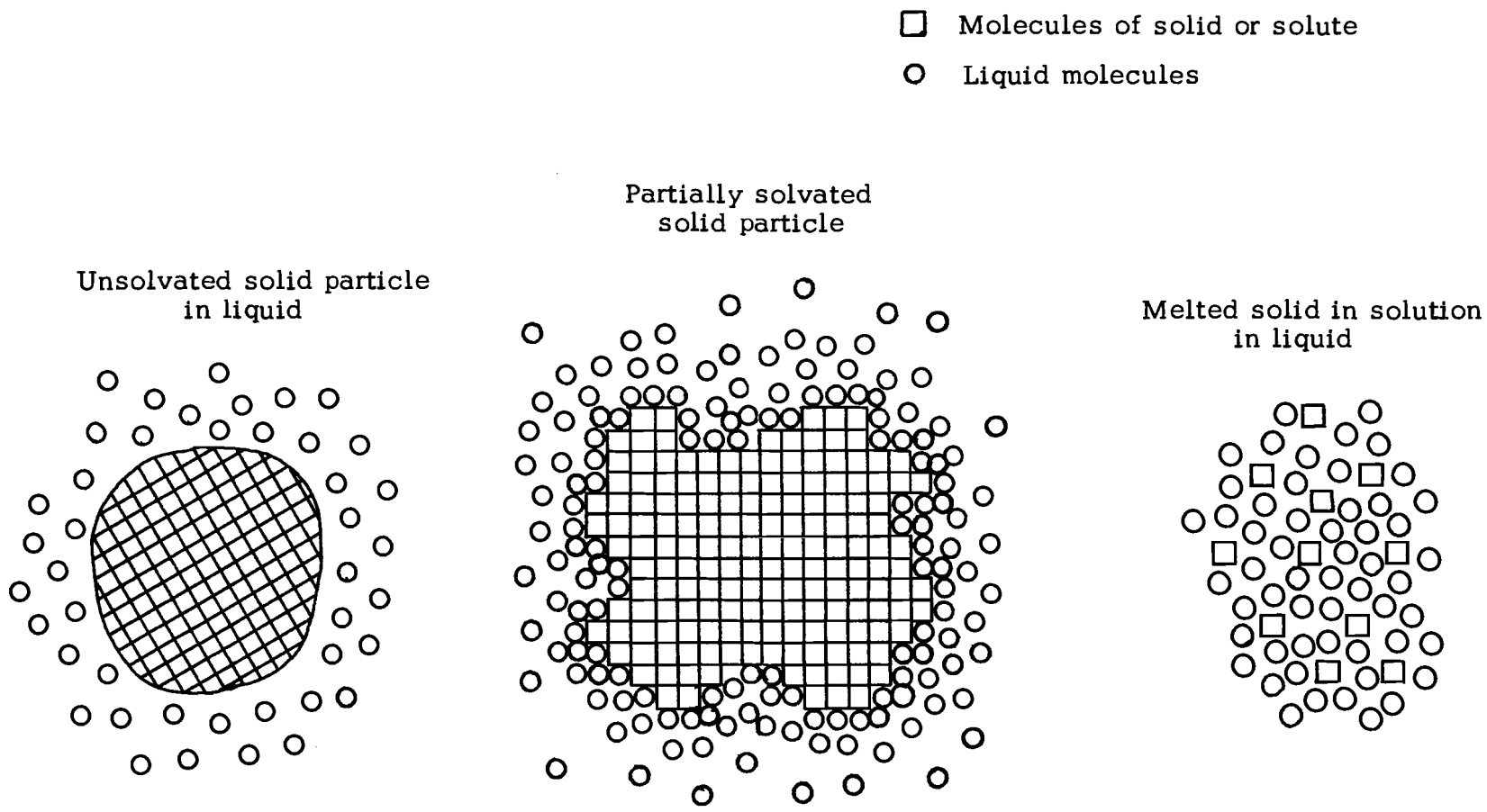

FIGURE 13

Partial Solvation as Found in Cooling Gel Formation

bound to surfaces. Silica gel and clays have polar surfaces. These surfaces can be made to adsorb hydrocarbons by pre-adsorbing polar molecules containing a hydrocarbon chain. The hydrocarbon ends stick out away from the surface and can solvate in more hydrocarbons. Thus, the particle of solid can form a sheath of hydrocarbon.

In the broadest sense, all gelling processes could be considered solvent effects, but this term is reserved for situations where the solvent properties are varied rather than the properties of the solute. Actually, both actions may occur simultaneously and the distinction is not always clear.

The type of gelling process chosen for aircraft fuel gelling determines the nature of the operations required in actual applications. The addition or removal of heat such as required by heating or cooling formed gels is a simple, easily controlled process. The addition of non-solvent is also an easily controlled process. Processes involving in situ chemical reactions are more critical, sensitive to temperature and more difficult to control. These factors do not rule out the use of gels formed by in situ reactions for aircraft fuels, but must be considered in the areas of ground handling of gelled fuels and techniques of preparation.

APPENDIX B

PRODUCT COMPOSITION AND SOURCES

SECTION 1
(Refers to Table I)

Product	Source	Composition
Armeen 18D	Armour	93% octadecylamine 6% hexadecylamine Combining M.W. 276
Armeen 16D	Armour	90% hexadecylamine 6% octadecylamine 4% octadecenylamine Combining M.W. 252
Armeen 14D	Armour	90% tetradecylamine 4% dodecylamine 4% hexadecylamine Combining M.W. 220
Armeen 12D	Armour	90% dodecylamine 9% tetradecylamine Combining M.W. 191
Armeen 10D purified grade (distilled)	Armour	90% decylamine 7% dodecylamine Combining M.W. 162
Armeen 8D purified grade (distilled)	Armour	90% octylamine 7% decylamine Combining M.W. 133
Armeen TD (tallow amine) purified grade (distilled)	Armour	30% hexadecylamine 25% octadecylamine 45% octadecenlyamine Combining M.W. 271
Armeen HTD	Armour	70% octadecylamine 25% hexadecylamine 5% octadecenylamine Combining M.W. 272
Armeen CD coco amine purified grade (distilled)	Armour	47% dodecylamine 18% tetradecylamine 9% decylamine 8% octylamine 8% hexadecylamine 5% octadecylamine 5% octadecenylamine Combining M.W. 206

SECTION 2
(Refers to Table II)

Product	Source	Composition
Armeen 2C coco amine	Armour	47% dodecylamine 18% tetradecylamine 10% octyldecylamine 9% decylamine 8% octylamine 8% hexadecylamine Combining M.W. 450
Armeen 2HT	Armour	75% octadecylamine 24% hexadecylamine 1% octadecenylamine Combining M.W. 530
Armeen 2S	Armour	35% octadecadienylamine 25% octadecenylamine 20% hexadecylamine 20% octadecylamine Combining M.W. 530
Armeen Z (formerly "Zwitterion")	Armour	N-coco beta amino butyric acid (Reaction product of primary coco amine and crotonic acid)
Armeen SZ	Armour	sodium salt of Armeen Z (N-coco beta amino butyric acid)
Armeen DM12D	Armour	dimethyl lauryl amine Apparent M.W. 213-224. 95% tertiary amine
Armeen DM14D	Armour	dimethyl myristyl amine Apparent M.W. 241-253
Armeen DM16D	Armour	dimethyl palmityl amine Apparent M.W. 269-283
Armeen DM18D	Armour	dimethyl stearyl amine Apparent M.W. 297-312
Armeen DMCD	Armour	dimethyl coco amine (principally lauryl, myristyl and capryl amines) Apparent M.W. 228-240
Armeen DMSD	Armour	dimethyl soybean derived alkyl amine (principally lioleyl, oleyl, stearyl and myristyl amines) M.W. 292-307

SECTION 2 (Continued)

Product	Source	Composition
Armeen DMHTD	Armour	dimethyl hydrogenated tallow amine (principally stearyl and myristyl amines) M.W. 293-308

SECTION 3
(Refers to Table III)

Duomeen C	Armour	N-coconut derived alkyl-trimethylene diamine (lauryl, myristyl, and capryl trimethylene diamines) M.W. 303 (80% active)
Duomeen CD	Armour	Purified Duomeen C (distilled)
Duomeen S	Armour	N-soya derived alkyl-trimethylene diamines (principally linoleyl, oleyl, stearyl and myristyl trimethylene diamines. Apparent M.W. 402 (80% active)
Duomeen T	Armour	N-tallow derived alkyl trimethylene diamine. Principally oleyl, stearyl, and myristyl trimethylene diamines. Apparent M.W. 400 (80% active)
Duomeen C-50	Armour	Duomeen C (coconut trimethylene diamine) 50% in isopropanol
Duomeen CD-50	Armour	Duomeen CD (distilled coconut trimethylene diamine) 50% in isopropanol
Duomeen O	Armour	N-oleyl trimethylene diamine 80% diamines
Oxy bis N,-N-Diethylamine	Dow Chemical	
Duomeen TDO	Armour	dioleate salt of Duomeen T (N-tallow derived alkyl trimethylene diamines)
Duomeen TMO	Armour	mono oleate salt of Duomeen T (N-tallow trimethylene diamine)

SECTION 3 (Continued)

Product	Source	Composition
Duomeen CDA-50	Armour	diadipate salt of Duomeen C (coco trimethylene diamine) 50% active (25% water, 25% hexylene glycol)

SECTION 4
(Refers to Table IV)

Ethomeen C/15	Armour	coco amine ethoxylated with 5 moles ethylene oxide per mole
Ethomeen C/20	Armour	coco amine ethoxylated with 10 moles ethylene oxide per mole
Ethomeen C/25	Armour	coco amine ethoxylated with 15 moles ethylene oxide per mole
Ethomeen S/15	Armour	soya amine ethoxylated with 5 moles ethylene oxide per mole
Ethomeen T/12	Armour	tallow amine ethoxylated with 2 moles ethylene oxide per mole
Ethomeen O/15	Armour	oleyl amine ethoxylated with 5 moles ethylene oxide per mole

SECTION 5
(Refers to Table V)

Dytol B-35	Rohm & Haas	61.2% lauryl alcohol
Dytol J-68	Rohm & Haas	81.5% lauryl alcohol
Dytol L-79	Rohm & Haas	99% lauryl alcohol
Dytol L-80	Rohm & Haas	99.1% lauryl 0.9% myristyl alcohols
Dytol R-52	Rohm & Haas	97.6% myristyl 0.6% lauryl 1.8% cetyl alcohols
Dytol F-11	Rohm & Haas	98.2% cetyl 0.6% stearyl 1.1% myristyl 0.1% lauryl alcohol

SECTION 5 (Continued)

Product	Source	Composition
Dytol E-46	Rohm & Haas	35.6% cetyl alcohol 64.4% stearyl alcohol

SECTION 6
(Refers to Table VI)

Armeen 8D	Armour	92% n-octylamine
Armeen 10D	Armour	90% n-decylamine
Armeen 12D	Armour	97% n-dodecylamine
Armeen 14D	Armour	90% n-tetradecylamine
Armeen 16D	Armour	76% n-hexadecylamine 12% n-tetradecylamine 10% n-octadecylamine
Armeen HTD	Armour	62% n-octadecylamine 30% n-hexadecylamine
Armeen 18D	Armour	85% n-octadecylamine 12% n-hexadecylamine
Armeen TD	Armour	37% n-octadecenylamine 29% n-hexadecylamine 23% n-octadecylamine
Armeen SD	Armour	49% n-octadecenylamine 25% n-hexadecylamine 15% octadecadienylamine
Armeen CD	Armour	53% n-dodecylamine 19% n-tetradecylamine 8% n-hexadecylamine

SECTION 7
(Refers to Table VII)

butyrolactone	General Aniline and Film Corp.	
N-octyl-γ-hydroxy-butyramide		Reaction product of butyrolactone and n-octylamine
N-decyl-γ-hydroxy-butyramide		Reaction product of butyrolactone and n-decylamine

SECTION 7 (Continued)

Product	Source	Composition
N-dodecyl-γ-hydroxy-butyramide		Reaction product of butyrolactone and n-dodecylamine
N-tetradecyl-γ-hydroxy-butyramide		Reaction product of butyrolactone and n-tetradecylamine
N-hexadecyl-γ-hydroxy-butyramide		Reaction product of butyrolactone and n-hexadecylamine
N-octadecyl-γ-hydroxy-butyramide		Reaction product of butyrolactone and n-octadecylamine
N-heavy tallow-γ-hydroxy-butyramide		Reaction product of butyrolactone and Armeen HTD (Armour)
N-tallow-γ-hydroxy-butyramide		Reaction product of butyrolactone and Armeen TD
N-coco-γ-hydroxy-butyramide		Reaction product of butyrolactone and Armeen CD

SECTION 8
(Refers to Table VIII)

Butoxyne 160	General Aniline and Film Corp.	N-coco derived akyl-γ-hydroxybutyramide
Fatty acid	Armour	(Neofat 140) A mixture of 55% linoleic, 43% oleic and 1% saturated fatty acids

SECTION 9
(Refers to Table IX)

Armid 8	Armour	93% octanamide 4% decanamide 3% hexanamide
Armid HT	Armour	75% octadecanamide 22% hexadecanamide 3% 9-octadecenamide
Armid C	Armour	49% dodecanamide 17% tetradecanamide 9% hexadecanamide 8% octadecanamide 7% decanamide (continued)

SECTION 9 (Continued)

Product	Source	Composition
Armid C (continued)		6% 9-octadecenamide 2% 9-12 octadecadienamide 2% octadecanamide
Armid 12	Armour	95% dodecanamide 4% tetradecanamide
Armid 14	Armour	94% tetradecanamide 3% dodecanamide 3% hexadecanamide
Armid 16	Armour	90% n-hexadecanamide 6% n-octadecanamide 4% 9-octadecenamide
N-tert-butyl-acrylamide	American Cyanamid Company	
Cyanogum 41	American Cyanamid Company	A mixture of arcylamide and N,N'-methylene bis-acrylamide
Acrylamide	American Cyanamid Company	
Polyacrylamide 50	American Cyanamid Company	MW $\sim$ 400,000
Polyacrylamide 75	American Cyanamid Company	MW $\sim$ 700,000
Polyacrylamide 100	American Cyanamid Company	MW $\sim$ 1,000,000
Nitrilotrispro-pionamide	American Cyanamid Company	β, β', β'' Nitrilotrispropionamide $N(CH_2CH_2CONH_2)_3$

SECTION 10
(Refers to Table X)

Zinc stearate	technical grade
Sodium hydroxystearate	technical grade

SECTION 10 (Continued)

Product	Source	Composition
Magnesium stearate		technical grade
Aluminum octoate		technical grade
Aluminum palmitate		technical grade

SECTION 11
(Refers to Table XI)

Dytol B-35	Rohm & Haas	61.2% lauryl alcohol
Dytol J-68	Rohm & Haas	81.5% lauryl alcohol
Dytol L-79	Rohm & Haas	99% lauryl alcohol
Dytol L-80	Rohm & Haas	99.1% lauryl alcohol
Dytol R-52	Rohm & Haas	97.6% myristyl alcohol
Dytol F-11	Rohm & Haas	98.2% cetyl alcohol
Dytol E-46	Rohm & Haas	35.6% cetyl alcohol 62.4% stearyl alcohol

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