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A Preliminary Report on The Storage Characteristics and Stability of Safety Fuels

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AUTHORIZATION

1. This problem was authorized by Bureau of Aeronautics Project Order 1-39 of 13 June 1938.

STATEMENT OF THE PROBLEM

2. This study is undertaken to examine the stability characteristics of several typical safety fuels now available commercially or potentially available in commercial quantities should a demand for them arise. In this report are given the characteristics of such fuels as are now in storage at this Laboratory and represent the characteristics of these fuels as received from the manufacturer or vendor, and as of January, 1941. They are being subjected to long time storage in containers of various metals in contact with salt water, or dry. From time to time, these fuels will be examined for changes in original characteristics in order to determine the degree of deterioration during storage.

PREVIOUS WORK DONE ON THE PROBLEM

3. This Laboratory has submitted reports Nos. P-1224, 1393, and 1481, which describe a similar storage of aviation gasoline.

KNOWN FACTS BEARING ON THE PROBLEM

4. By far the majority of power plants for aircraft utilize low-flash, low boiling, high vapor pressure fuels (gasoline), though in the last few years in this country and especially in some of the foreign Services, much interest has been evinced in heavier fuels of comparatively low vapor pressure, high boiling range and of flash points above usual atmospheric temperatures. The most noteworthy advantage of such fuels lies in the high flash point (in excess of 100° F) which minimizes the danger of accidental fires hazardous to life and matériel. High flash fuels should make storage depots more secure, and should decrease danger of fire when fuel is spilled in crashes or when tanks are punctured in combat or otherwise damaged in military operations. Because the vapor pressure of these high flash fuels is low, the vapor from the spilled fuel will not form explosive mixtures with air as readily as will gasoline released under the same conditions, and a flame once started will have a lessened tendency to propagate itself. Therefore, inflammation from sparks or small fires can be more easily controlled. Because of these properties, such fuels have been called "safety fuels," or "safety gasolines."

5. Except for a difference in such physical properties as boiling range, volatility, and flash point, safety fuels are closely related to the more familiar gasolines, the basic difference being that the average molecular weight of the component hydrocarbons of the former is higher than of the latter. Because of this similarity of composition, the service behavior of these safety fuels could be expected to parallel that of gasoline, varying only in such degree as the properties of the higher molecular

weight hydrocarbons of safety fuel differ from the lighter species present in gasoline. In this connection, this Laboratory has some evidence (Naval Research Laboratory Report No. P-1527, "The Oxidation and Gumming Tendency of Certain Typical Component Hydrocarbons of Aviation Gasoline") that with increases in complexity, certain types of hydrocarbons, chiefly representatives of the naphthenic and aromatic series, show decreased stability toward oxygen and probably decreased storage stability. Therefore, in connection with the studies of commercial safety fuels stored under conditions simulating those of Naval practice, an investigation is being made of the bomb oxidation of certain pure hydrocarbons boiling in the range of these safety fuels in order to relate their behavior with the long-time storage of the fuels themselves. Data for a report on the results of these oxidations are being collected.

THEORETICAL CONSIDERATIONS

6. The advantages of safety fuels as propellents for Fleet aircraft may be listed as follows:

(1) Decreased fire hazard. Safety fuels are obtainable with a flash point of 100-130° F. Explosive mixtures are not likely to be encountered in the vicinity of storage depots or in confined spaces such as the under-deck of carriers, since temperatures above 100° F are encountered only infrequently in these locations. Increased safety in plane operation have been indicated.

(2) Available safety fuels have octane ratings and lead susceptibilities comparable with and equal to grades of gasoline and base stocks now being supplied under current specifications. The substitution of high flash fuels for gasoline need not be made with an octane number penalty.

(3) Newer safety fuels are comprised mainly of branched chain aliphatic hydrocarbons and resemble quite closely the paraffinic type gasolines now used to the practical exclusion of any other in the military aircraft of this country. The engine performance of these safety fuels should approximate that of these gasolines.

(4) Though safety fuels, because of low volatility, are not readily carbureted, these fuels can be utilized by installation of proper injection equipment. The following advantages accrue for safety fuels so utilized:

(a) The charge per cylinder can be metered exactly. In this way each cylinder can be made to burn the optimum mixture for power generation, and no cylinder need be fed a mixture too rich or too lean. Thus, some fuel economy may be anticipated and fuller advantage may be taken of the anti-knocking qualities of the fuel.

(b) Engine operation in unusual positions, inverted flight sometimes necessary in maneuvers, is more certain than with carburetor feeds and air induction systems.

(5) The low volatility of safety fuels should be reflected in a lowered tendency to vapor locking and in lowered volatilization loss during storage periods.

(6) The available heat content of paraffinic safety fuels compares with aviation gasoline both on a weight and gallonage basis. This is not true, however, for high aromatic fuels.

The main factors militating against the use of safety fuels are:

(1) Modification of existing equipment would be necessitated by installation of injection systems and appropriate accessories.

(2) Proper design for engines to utilize the full advantage derivable from propellents of the safety fuel type is still somewhat unsettled.

(3) The supply of such fuels in definitely limited at present, though it could be considerably increased by plant expansion contingent on demand.

(4) The autogenous ignition temperature, or the temperature of spontaneous inflammation when dropped upon a heated surface, is somewhat lower for some safety fuels than for some selected gasolines. This difference is not great and becomes of minor importance when it is realized that explosive mixtures do not generally form within areas of safety fuel spillage, but almost invariably exist where gasoline is spilled. Hence, in crashes the spontaneous ignition of gasoline dropped on a hot exhaust pipe or falling on heated engine parts is likely to be accompanied by inflammation and vigorous combustion of all escaped gasoline in the vicinity, where with safety fuel the blaze will be largely localized..

METHODS

7. The several fuels herein discussed were collected over a period of two years. In all cases, the original characteristics of the fuels as received are given and the characteristics as of January, 1941, together with the properties as determined by the vendor before shipment, where such data are available. Since these fuels have been kept in the original containers, change in the properties is indicative of drum and can storage stability. The following characteristics of fuels have been determined:

(1) Gum. ASTM designation D-381-36. 50cc of test fuel were evaporated in a tared glass beaker at 157° C. in a blast of air flowing at a rate of one liter per second and weighed.

(2) Autogenous Ignition Temperatures. ASTM designation D-286-30. The temperature of spontaneous ignition was determined by dropping the fuel into 125 cc glass Erlenmeyer flask heated to the ignition temperature by a solder bath. The method is essentially that of the American Society for Testing Materials, but some modifications have been introduced which will be described in detail at an early date in a report on the autogenous ignition temperatures of pure hydrocarbons boiling in aviation gasoline and safety fuel range.

(3) Distillation. ASTM D-86-40.

(4) Tetraethel lead. ASTM D-526-39T. Lead was determined by refluxing a 50 cc sample of fuel with an equal volume of concentrated hydrochloric acid in an expecially designed apparatus, quantitatively withdrawing the acid layer, evaporating it, and analyzing the residue for lead gravi-metrically as the chromate.

(5) Flash point. Flash points were determined in a Tag closed tester exactly as described in ASTM designation D-93-40.

(6) Gravity, Refractive Index. The gravities of the samples were taken with standard API hydrometers and expressed both as API gravity and specific gravity. Refractive index was determined with an Abbe refractometer at 25° C.

(7) Accelerated oxidation. Bomb oxidations were run in ASTM bombs both by a modified Army method with iron, and a 24-hour oxidation without iron.

DATA OBTAINED (See Tables)

TABLE 1

Inspections of Houdry Safety Fuel, Socony Vacuum Oil Company, 5 Gallon Sample, Received December 1938.

Characteristics of Fuel	As Determined by Vendor*	As Received NRL	As of Jan. 1941
Color	–	Yellow	Yellow
Gravity, API(60°F)	–	35.8	35.8
Gravity, specific (60°F)	–	0.8458	0.8458
Aniline Point, C°	–	29.4	19.4
Flash Point, F°	–	–	119.0
Autogenous Ignition Temperature, C°(F°)	–	–	375 (707)
Gum, preformed, mg/100 cc	–	1.2	10.2
Gum, potential, Army	–	–	79.8
Gum, 24 hour oxidation without iron	–	14.0	31.6
Distillation Initial, F°	–	333	332
10% recovery	–	340	342
20%	–	–	345
50%	–	354	354
80%	–	–	368
90%	–	378	377
End point	–	400	398
cc TEL/gallon	–	None	None
Refractive Index 25/D	–	1.4672	1.4680

*Information not available.

TABLE 2

Inspections of Texas Oil Company Safety Fuel
(55 gallon drum, Serial 291894) Received February 1940

Characteristics of Fuel	As Determined by Vendor*	As Received NRL	As of Jan. 1941
Color	-	White	White
Gravity, API(60°F)	-	57.7	57.7
Gravity, specific(60°F)	-	0.7479	0.7479
Aniline point, C°	-	83.4	83.60
Flash point, F°	-	-	100.5
Autogenous ignition Temperature, C°(F°)	-	-	381(718)
Gum, preformed, mg/100 cc	-	1.0	1.0
Gum, potential, Army	-	-	0.8
Gum, 24 hour oxidation without iron	-	1.2	-
Distillation, Initial, F°	-	312	310
10% recovery	-	324	325
20%	-	329	330
50%	-	340	341
80%	-	353	354
90%	-	360	361
End point	-	386	385
cc TEL gallon	-	None	None
Refractive index $^{25}_{D}$	-	1.4158	1.4160

*Information not available.

TABLE 3

Inspections of Texas Oil Company Sample D-64,
55 Gallon Drum, Received May 1939

Characteristics of Fuel	As Determined by Vendor*	As Received NRL	As of Jan. 1941
Color	–	White	White
Gravity, API(60°F)	–	55.9	55.9
Gravity, specific (60°F)	–	0.7551	0.7551
Aniline Point, C°	–	79.80	80.05
Flash Point, F°	–	–	94
Autogenous Ignition Temperature, C°(F°)	–	–	343(649)
Gum, preformed, mg/100 cc	–	0.4	0.6
Gum, potential, Army	–	–	1.6
Gum, 24 hour oxidation without iron	–	1.0	–
Distillation, Initial, F°	–	298	296
10% recovery	–	318	320
20%	–	326	329
50%	–	348	350
80%	–	370	369
90%	–	380	380
End point	–	410	409
cc TEL/gallon	–	–	None
Refractive index $\frac{25}{D}$	–	1.4200	1.4208

*Information not available.

TABLE 4

Inspections of Texas Oil Company Safety Fuel D-38
5 Gallon Sample - Received Late in 1938

Characteristics of Fuel	As Determined by Vendor*	As received NRL	As of Jan. 1941
Color	-		White
Gravity, API(60°F)	-	57.1	57.30
Gravity, specific (60°F)	-	0.7503	0.7495
Aniline point, C°	-	81.5	81.75
Flash point, F°	-	-	87.5
Autogenous ignition			
Temperature, C° (F°)	-	-	370 (698)
Gum, preformed, mg/100 cc	-	0.6	0.2
Gum, potential, Army	-	-	4.4
Gum, 24 hour oxidation		-	-
without iron	-	14.0	-
Distillation, Initial, F°	-	290	284
10% recovery	-	313	310
20%	-	321	320
50%	-	345	343
80%	-	367	366
90%	-	379	378
End point	-	409	405
cc TEL/gallon	-	None	None
Refractive index $\frac{25}{D}$	-	1.4194	1.4180

*Not available.

TABLE 5

Inspections on Shell Oil Company Safety Fuel,
5 Gallon Sample, Code 1175, Received May 1940

Characteristics of Fuel	As Determined by Vendor	As Received NRL	As of Jan. 1941
Color	Blue		Blue
Gravity, API (60°F)	56.7	56.8	56.8
Gravity, specific (60°F)	0.7507	0.7515	0.7515
Aniline point, C°	-	83.30	83.50
Flash point, F°	110	-	105
Autogenous ignition Temperature, C° (F°)	-	-	460 (860)
Gum, preformed, mg/100 cc	2.5*	1.4	1.2
Gum, potential, Army	-	-	3.0
Distillation, Initial, F°	324	318	317
10% Recovery	331	330	329
20%	334	333	332
50%	342	341	342
80%	352	353	355
90%	357	359	360
End point	369	371	370
cc TEL/gallon	3.0	2.94	2.91
Refractive index $\frac{25}{D}$	-	1.4169	1.4174

*Copper dish gum

TABLE 6

Inspections of Shell Oil Company Safety Fuel, Code 1175R
5 Gallon Sample, received August, 1940

Characteristics of Fuel	As Determined by Vendor	As Received NRL	As of Jan. 1941
Color	Blue	Blue	Blue
Gravity, API (60°F)	54.0	54.1	54.4
Gravity, specific(60°F)	0.7628	0.7624	0.7612
Aniline point, C°	-	81.60	81.60
Flash point, F°	111	-	110
Autogenous ignition Temperature C° (F°)	-	-	461 (862)
Gum, preformed, mg/100 cc	4*	1.0	1.2
Gum, potential, Army		-	3.0
Distillation, Initial, F°	328	328	331
10% recovery	339	342	343
20%	-	345	345
50%	350	352	353
80%	-	361	360
90%	362	363	364
End point	378	380	380
cc TEL/gallon	2.90	2.90	2.94
Refractive index $^{25}_{D}$	-	1.4222	1.4226

*Copper dish gum

TABLE 7

Inspections on Shell Oil Company Safety Fuel
55 Gallon Drum, Code 1175-W, Received August 1940

Characteristics of Fuel	As Determined by Vendor	As Received NRL	As of Jan. 1941
Color	Blue	Blue	Blue
Gravity, API (60°F)	55.5	55.5	55.5
Gravity, specific (60°F)	0.7567	0.7567	0.7567
Aniline Point, C°	-	86.30	86.35
Flash point, F°	124	-	114.5
Autogenous ignition Temperature, C° (F°)	-	-	478 (892)
Gum, preformed, mg/100 cc	-	0.6	0.8
Gum, potential, Army	-	-	0.8
Distillation, Initial, F°	340	342	342
10% recovery	345	346	346
20%	-	348	347
50%	347	349	349
80%	-	350	350
90%	349	351	352
End point	362	361	362
cc TEL/gallon	2.95	2.90	2.82
Refractive index n_D^{25}	-	1.4196	1.4200

TABLE 8

Inspections of Standard Oil of Louisiana Safety Fuel
55 Gallon Drum, Received October 1940

Characteristics of Fuel	As Determined by Vendor	As Received NRL	As of Jan. 1941
Color	-		
Gravity, API (60°F)	0.7543	0.7527	0.7527
Aniline Point, C°		83.5	83.65
Flash point, F°	108	-	105.0
Autogenous ignition Temperature, C° (F°)	-	-	458 (856)
Gum, preformed, mg/100 cc	1.0	1.0	0.8
Gum, potential, Army	-	-	3.4
Distillation, Initial, F°	322	319	320
10% Recovery	332	331	332
20%	335	335	337
50%	343	342	343
80%	354	354	354
90%	360	361	360
End point	383	383	380
cc TEL/gallon	3.39	3.42	3.40
Refractive index $\frac{25}{D}$	-	-	1.4174

TABLE 9

Inspections on Standard Oil of Louisiana Paraffinic Safety Fuel, H-EL-40-159-2, Base Stock, Without Lead, 5 Gallon Sample, Received March 1940

Characteristics of Fuel	As Determined By Vendor	As Received NRL	As of Jan. 1941
Color	White	White	White
Gravity, API (60°)	57.7	57.8	57.80
Gravity, specific (60°F)	0.7479	0.7475	0.7475
Aniline point, C°	83.3	83.0	82.8
Flash point, F°	102	–	101
Autogenous ignition Temperature, C° (F°)	–	–	383 (721)
Gum, preformed, mg/100 cc	1.2*	0.6	0.4
Gum, potential, Army	1.6	–	4.0
Distillation, Initial, F°	315	312	313
10% Recovery	322	321	322
20%	324	323	325
50%	332	333	333
80%	343	344	344
90%	349	353	352
End point	381	370	369
cc TEL/gallon	None	None	None
Refractive index $\frac{25}{D}$	–	1.4150	1.4158

*Copper dish gum

TABLE 10

Inspections on Paraffinic Safety Fuel, Leaded, 5 Gallon Sample, H-EL-40-159-1, Received March 1940

Characteristics of Fuel	As Determined by Vendor	As Received NRL	As of Jan. 1941
Color	Blue	Blue	Blue
Gravity, API (60°F)	57.3	57.4	57.40
Gravity, specific (60°F)	0.7495	0.7491	0.7491
Aniline point, C°	82.8	82.75	82.70
Flash point, F°	101	-	100
Autogenous ignition Temperature, C° (F°)	-	-	460 (860)
Gum, preformed, mg/100 cc	1.6*	0.8	1.0
Gum, potential, Army	2.8	-	3.8
Distillation, Initial, F°	315	314	314
10% Recovery	322	323	322
20%	324	224	324
50%	332	332	333
80%	343	345	344
90%	349	350	352
End point	381	369	368
cc TEL/gallon	3.46	3.50	3.59
Refractive index $\frac{25}{D}$	-	1.4152	1.4160

*Copper dish gum

CONCLUSIONS

8. Of the ten fuels examined, nine are paraffinic in type, composed chiefly of hydrocarbons of the paraffin and possibly the naphthene series, and are low in aromatics. One fuel, described in Table 1, contains large quantities of aromatics as evidenced by the low aniline point and high refractive index. This particular fuel, product of Socony Vacuum Oil Company, is one of the older samples from the standpoint of time elapsed since receipt at this Laboratory. It is interesting to note that after storage for twenty-four months in the original container (a five-gallon tin can) this fuel is beginning to show definite signs of instability on long-time storage. When originally received, the fuel was low in preformed gum, though it had a potential gum of 14 milligrams on 24-hour oxidation. It was free of organic peroxides, the appearance of which in hydrocarbon fuels usually heralds incipient gumming. During the storage period, the preformed gum has risen to 10 milligrams per 100 cc, and potential gum (Army: oxidation in the presence of iron strips for five hours) is about 80 milligrams. Twenty-four-hour oxidation without iron yields about 30 milligrams per 100 cc. The stored fuel now gives heavy test for peroxides. A puzzling drop in aniline point from 29°C to 19°C was noted. No obvious explanation for this occurrence is at once apparent unless the presence of oxidation products in the stored fuel increases the mutual solubility of the fuel and aniline. The effect of hydrocarbon oxidation products on the aniline point of the parent hydrocarbons should be investigated.

Only one other fuel compares in age with the Socony Vacuum sample; namely, Texas Company D-38 (see Table 4). This fuel, of high aniline point and comparatively low refractive index is, as has been stated, predominantly paraffinic in type. The stability characteristics of this fuel are definitely superior to the aromatic type both on long-time storage and accelerated oxidation.

9. The other fuels, ranging in storage age from 18 months to 3, show no changes that may be interpreted as storage instability during the respective period that each has been kept. Preformed gums are in all cases low and Army gum values do not exceed 5 milligrams per 100 cc. No evidence of atmospheric oxidation nor peroxidic bodies in the fuel were noted. These fuels are being stored over sea water or in dry storage vessels in containers fabricated of various metals in order to determine what, if any, deterioration takes place under conditions paralleling Naval storage practices.

10. In connection with the data, the results of the inspections of the fuels described in Tables 2 through 10 show good agreement among themselves in respect not only to the original inspections and those of January, 1941, but also between the original inspections of this Laboratory and those of the vendor where such data are available. The greatest variance in the findings of this Laboratory as compared with those of the manufacturers, is in the matter of flash points, for which Naval Research Laboratory findings are lower than those reported by the vendors. It will be noted that except in the case of Texas Company D-38 and the drum sample described

in Table 3, all flash points are above 100° F. These fuels should, therefore, be much less subject to accidental ignition than ordinary gasolines which may flash as low as -40° F.

11. The autogenous ignition temperatures, or the points where spontaneous ignition in the absence of an open flame takes place when the fuel is dropped upon a heated suface, are not significantly different from gasoline. The effect of tetraethyl lead on the spontaneous ignition temperature is pronounced. For example, the fuel described in Table 10 differs from that in Table 9 only by the addition of tetraethyl lead. Yet the spontaneous ignition point of the former is 140° F above that of the latter.* The addition of tetraethyl lead to the unleaded fuels described in Tables 1 through 5 gave the following results:

Fuel	Spontaneous Ignition Temperature, C° (F°) Without lead	+ 3cc TEL/Gal.	Increase
Table 1, Soc. Vac.	375 (707)	445 (833)	70 (126)
Table 2, Texas Co.	381 (718)	484 (903)	103 (185)
Table 3, Texas Co.	343 (649)	445 (833)	102 (184)
Table 4, Texas Co.	370 (698)	472 (882)	102 (184)

Ethylene dibromide, used in conjunction with lead tetraethyl in leaded gasolines, apparently does not contribute to the increase in self-flashing temperature. After the addition of 3 cc/gallon of ethylene dibromide to Texas Co. D-38 clear base stock, the autogenous ignition temperature of the blend was the same as originally found. These data indicate that leaded fuels spontaneously ignite less readily than do unleaded ones, which would suggest that fuels containing lead have a higher safety factor than the corresponding clear base stocks and are less prone to spontaneous inflammation when released upon hot engine parts through accidental spillage in crashes or in military action.

*A similar effect has been noted by others. Sortman, Beatty, and Heron, "Spontaneous Ignition of Hydrocarbons and Zones of Non-Ignition", presented before the Symposium of Petroleum Chemistry at the Detroit meeting of American Chemical Society, September 9 - 13, 1940.

SUMMARY

(1) The drum and tin storage stability of ten safety fuels has been examined. Except for the fuel described in Table 1, these materials show no evidence of storage instability over the periods of three to twenty-four months that the several fuels have been kept at this Laboratory during collection of samples.

(2) The drum and can storage stability of paraffinic type fuels is superior to aromatic types. This is in accord with findings of this Laboratory in theoretical studies of the stability of certain pure hydrocarbons. However, it is realized that the premise of differing stabilities of highly paraffinic and highly aromatic safety fuels is based on the storage instability of but a single sample of a fuel of the latter type. Therefore, until a representative number of other aromatic rich

blends can be examined, such a conclusion is of course conditional.

(3) The flash points of eight of the fuels are above 100° F. while two are somewhat below that figure. It is not felt that fuels with flashing temperatures below 100° F. should be considered true safety fuels though the two fuels in question are probably much safer than ordinary gasoline from the standpoint of fire hazard. Based on the flash points of the two similar fuels described in Tables 9 and 10, one of which is leaded and the other clear, the addition of tetraethyl lead has little or no effect on the flash point.

(4) The autogenous ignition temperature of the safety fuels is not significantly different from gasoline. The fire hazard from spontaneous inflammation of fuel released on heated metal surfaces will not be greater with safety fuels than with gasoline. Tetraethyl lead definitely increases the autogenous ignition temperature.

RECOMMENDATIONS

It is recommended:

(1) That more samples of typical aromatic type fuels be investigated in order to compare the storage stability of the aromatic type with paraffinic and naphthenic types.

(2) That the storage stability of the fuels herein discussed over salt water or in dry containers and in vessels of various metals under conditions paralleling Naval storage practices be closely examined.

(3) That the effect of tetraethyl lead on the spontaneous ignition temperature be more fully investigated and the possibility of additives to raise the flash point of low flash fuels be considered.