(2) Gardner, H. A., "Physical and Chemical Examination of Paints, Varnishes and Lacquers," 11th ed., Henry A. Gardner Laboratory, Bethesda, Md., 1950.
(3) Modern Plastics Encyclopedia Issue, Vol. **35**, No. 1A, Plastics Catalogue Corp., Bristol, Conn., September 1957.
(4) Morrison, W. D., *Chem. Eng. News* **31**, 658–60 (1953).
(5) Orth, H. (to Dynamit-Actien-Gesselschaft), German Patent **852,301** (Oct. 13, 1952).
(6) Orth, H. (to Dynamit-Actien-Gesselschaft), U. S. Patent **2,687,407** (Aug. 24, 1954).
(7) Rothrock, H. S. (to E. I. du Pont de Nemours & Co), *Ibid.*, **2,401,776** (June 11, 1946).
(8) Rouse, J., *Offic. Dig. Federation Paint & Varnish Production Clubs* **346**, 825–39 (1953).
(9) Schulz, H., Wagner, H., U. S. Dept. of Commerce, Office of Pub. Board, Rept. **BB-70309** (Frames **8227–8231, 8303–8314**) (1944).
(10) Schulz, H., Wagner, H., *Angew. Chem.* **62**, 105–32 (1950).
(11) Shell Chemical Corp., "Epon Resin Formulation XA-200," Tech. Bul. **SC:52-39** (October 1952).
(12) Wagner, H. (to Deutsche Gold- und Silber-Scheideanstalt), German Patent **870,032** (March 9, 1953).

RECEIVED for review May 14, 1958. Accepted October 29, 1958.

Effect of Composition and Storage on the Properties of Jet Fuels

A. C. NIXON, C. A. COLE, and H. B. MINOR
Shell Development Co., Emeryville, Calif.

Most of the reactions which cause a fuel to fail from a stability standpoint involve oxygen, either dissolved or as oxygenated compounds formed as a result of previous reaction of atmospheric oxygen with fuel constituents. While this usually involves the hydrocarbon constituents of the fuel, very often minor amounts of nitrogen- and sulfur-containing compounds are involved in the degradation reactions. The end result of such reactions is the formation of soluble and insoluble gum which often causes malfunction of equipment.

STORAGE STABILITY

To meet the demands of military logistics the Air Force must maintain large supplies of jet fuel constantly in storage at various locations around the globe. This fuel must be of sufficient stability to be instantly available for use whenever needed. While the fuel can be kept relatively fresh in some areas by rotation of stocks, this expedient may be impractical in others. It is important then to know what factors contribute to instability and to determine whether the specification tests utilized are adequate to ensure sufficient stability. Jet fuels can, broadly speaking, be made from any hydrocarbon constitutents boiling in the range of roughly 150° to 600° F. One of the important restrictions on the composition of the jet fuel produced is the stability of the blend. Figure 1 shows the effect of desert drum storage on the total and insoluble gum content of four fuels prepared from Texas crudes at the same refinery. They all fall approximately in the JP-3 boiling range. The stability of the blends decreases in the order straight-run, catalytically cracked, thermally cracked, with the composite blend (made up of one third of each of the other fuels) behaving like the cracked samples. This type of behavior is typical of the general order of stability of these classes of fuels and is in agreement with the results of Schwartz, Ward, and Smith (*6*) for the stability of diesel fuels. The variations in the point to point slopes for different time intervals is not the result of experimental error. Characteristically, the rate of gum formation either slowed up during the winter months or the amount present actually decreased, probably because of plating out of the gum on the sides and bottom of the container.

The stability of fuels can be considerably improved by various refinery treatments. The fuels referred to above had all received conventional refinery treatments, but no particular effort was made to hold the treatments at a constant level for purposes of comparison. A laboratory study was made for this purpose (Figure 2). The authors' earlier work had shown that the controlling factor in the stability of a jet fuel was generally the stability of the gas oil portion, that is, the fraction boiling above about 400° F. Accordingly, straight-run, catalytically cracked, and thermally cracked gas oils were obtained from a California refinery; each was treated in various ways and then blended with a stable composite gasoline (⅓ straight-run, ⅓ catalytically cracked, and ⅓ thermally cracked) to make a simulated jet fuel. The fuels were then placed in storage at 110° F. in the presence of excess air.

Figure 2 shows the effects of the various laboratory treatments on the total gum formed after 6 months' storage. The

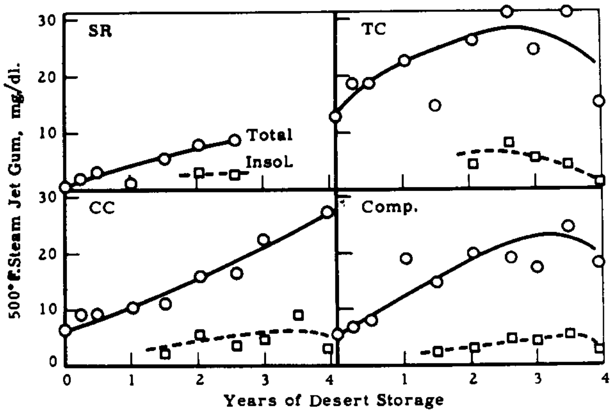

Figure 1. Effect of desert drum storage on the stability of jet fuels from Texas crudes

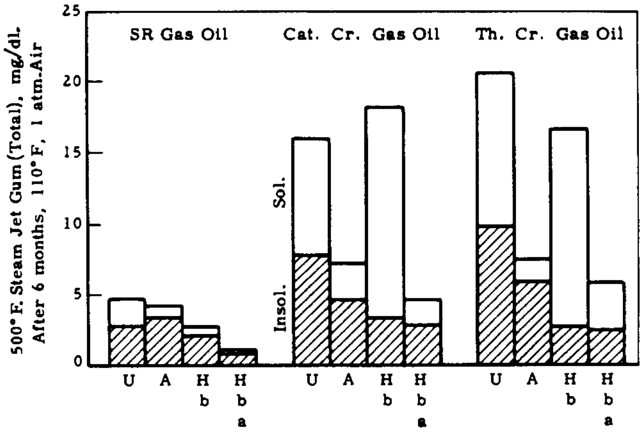

Figure 2. Effect of various treatments on formation of gum in laboratory storage

treatments used were: acid followed by caustic and redistillation (A), hydrogenation followed by caustic washing (Hb), and the same treatment followed by a dilute acid wash (Hba). In all cases the gas oil was distilled immediately before treatment. All the treatments (except Hb, catalytically cracked) had some favorable effect on the stability of the fuels. The most encouraging results were obtained by acid treatment and by hydrogenation (Hba). The acid treatment was an unusually heavy one (30 pounds per barrel of 93% sulfuric acid) while the hydrogenation was an extremely mild trickle phase treatment, being done at 750 p.s.i.g., 480° F. with 35 cu. ft. of hydrogen per barrel over a molybdenum sulfide–alumina catalyst. The marked effectiveness of the very dilute (2 weight %) sulfuric acid wash following hydrogenation is striking. The improvement was probably due to the removal of a small amount of nitrogen bases. The total nitrogen content was reduced from 0.05 and 0.04 to 0.01% for the catalytically cracked and thermally cracked gas oils respectively, by the dilute acid wash. It is unlikely that anything except bases would be removed by such dilute acid. It is evident that the quantity of available stocks for preparation of stable jet fuels can be markedly increased if the demand becomes sufficient. The components which are largely removed by the treatments mentioned above are diolefins and sulfur and nitrogen compounds. The deleterious effect of these components has been shown both analytically and synthetically. The separation of components by distillation and chromatography has shown that conjugated diolefins related to cyclopentadiene, aromatic olefins, substituted thiophenes, indenes, and carbazoles have strong gum-forming tendencies. The addition of model compounds to an otherwise stable fuel has shown that mercaptans, thiophenols, and pyrroles are active in the formation of gum (*3,5*).

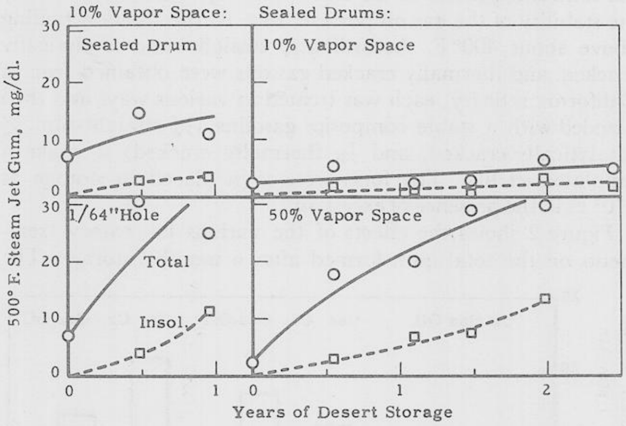

Figure 3. Effect of oxygen availability on gum formation during desert drum storage

This type of oxidation cannot occur unless oxygen is present. As far as strategic storage is concerned, one of the most important things which could be done would be to prevent the access of oxygen to fuel in storage. The effect of oxygen availability is illustrated by Figure 3, which shows, on the right side, the effect of storing a fuel in the desert, in one case with 10% air space and in another with 50% air space. The much higher rate of formation of both soluble and insoluble gum is clearly evident with the larger vapor space. While it would seem a simple matter to keep oxygen out of fuel containers, in actual practice, it is difficult to achieve. The left side of Figure 3 shows the result of an experiment designed to simulate the effect of having a poorly sealed drum by drilling a 1/64-inch hole through the cap. The rate of deterioration was very much greater in the case of the drum with the hole in it, despite the fact that very little loss of fuel occurred through this hole in the course of a year. The oxygen content inside the drum remained almost the same as that of the atmosphere. Of course, even with a well sealed drum the fuel will be initially saturated with oxygen and some air space will be present which will allow the formation of a modicum of deterioration products.

LOW AND AMBIENT TEMPERATURE FILTERABILITY

One effect of storage of jet fuels is the formation of insoluble gum which may or may not be augmented by rust, dirt, and water. To take care of the presence of such materials, aircraft designers and the Air Force have gone to considerable trouble to provide frequent and careful filtration at various points in the fuel handling system both on the ground and in the air. It is axiomatic that when a solid is filtered from a liquid, the filter tends to become plugged. However, not all solids plug filters at the same rate. It was a matter of considerable interest to see whether any rationale could be arrived at with respect to the properties of solids deposited from jet fuels and their effect on filter plugging. To determine the effect of insolubles on filterability it was necessary to develop an apparatus which would measure this function. The apparatus should have a small volume, in order to measure filterability on samples artificially aged in oxygen bombs. Constant flow is desirable, as this would more closely simulate actual aircraft operation. Furthermore, it was desired to be able to regulate the temperature over a wide range, so as to simulate operation at high altitude or latitude. The apparatus, illustrated in Figure 4, consists of a 100-ml. hypodermic syringe driven by a constant-speed motor which passes the test sample through a 10 micron aircraft-type filter paper. A magnetic stirrer within the syringe serves to keep the insoluble residue well dispersed. A mercury manometer records the change in pressure across the filter. The flow rate is about 13.5 ml. per minute, so the test requires only about 7.5 minutes. Spherical joints are employed for ease of assembly and disassembly. A glass heat exchanger may be used to control the temperature of the fuel at the filter at any point from about −100° to 212° F. The test has proved extremely useful, and the authors believe it is a reasonable representation of conditions that might be encountered in aircraft fuel systems. Figure 5 compares results obtained with this test and with Wright Air Development Center full-scale test. While the correspondence was not always as good as shown, in three out of five comparisons, results were substantially the same for the two types

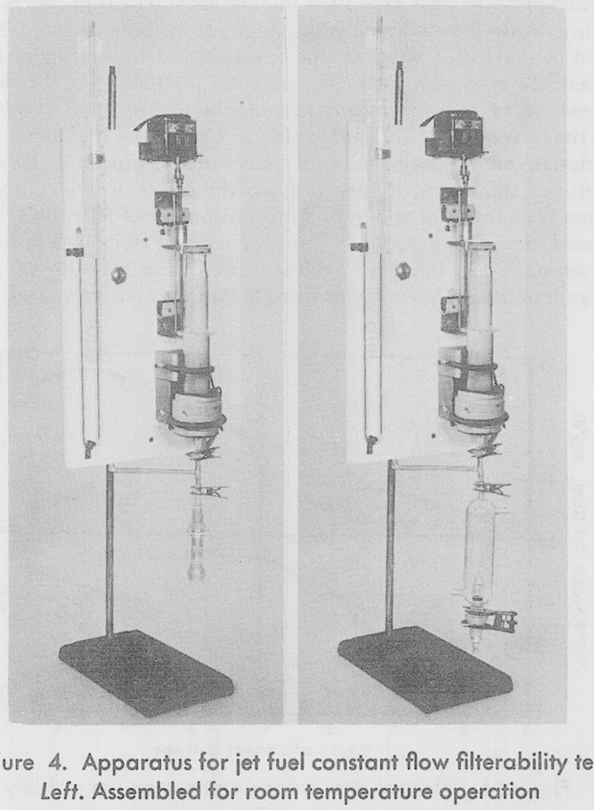

Figure 4. Apparatus for jet fuel constant flow filterability test
Left. Assembled for room temperature operation
Right. Assembled for low temperature operation

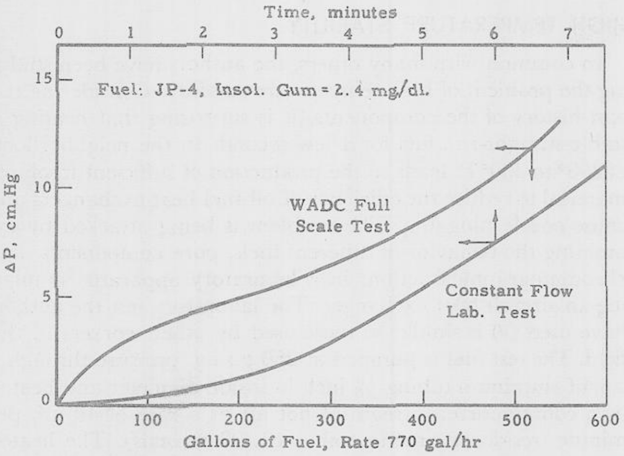

Figure 5. Comparison of bench and full scale filterability tests

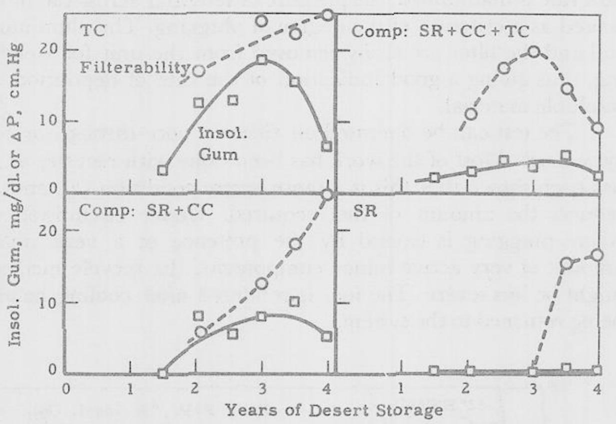

Figure 6. Effect of desert aging on insoluble formation and fuel filterability characteristics

of test. In the other two cases, the laboratory rating gave higher pressure drop readings than the full-scale test. However, in view of the difficulty of getting uniform samples of fuels containing insolubles, such results are not unexpected.

The next question was: Is the filter plugging tendency of the fuel proportional to the amount of insolubles it contains? The answer is, that it is not. Figure 6 shows the effect of desert aging at El Centro with respect to insoluble material and filterability for four JP-3 fuels. A wide variety of behaviors is illustrated. With a thermally cracked fuel, insoluble gum rose with storage time and then dropped off rapidly, probably because of the adherence of insolubles on the walls of the container. The pressure drop, however, continued to rise without regard for the amount of insoluble gum. Somewhat similar behavior was shown by the straight-run–catalytically cracked composite. With the three-ply composite, however, the insoluble gum rose very gradually with time while the filterability climbed up and then dropped off. The straight-run fuel illustrated in the lower right corner formed very little insoluble material over its entire storage history. For 3 years the filterability paralleled this behavior. At the end of that time, however, the filterability pressure drop suddenly increased to a high value for no superficially apparent reason.

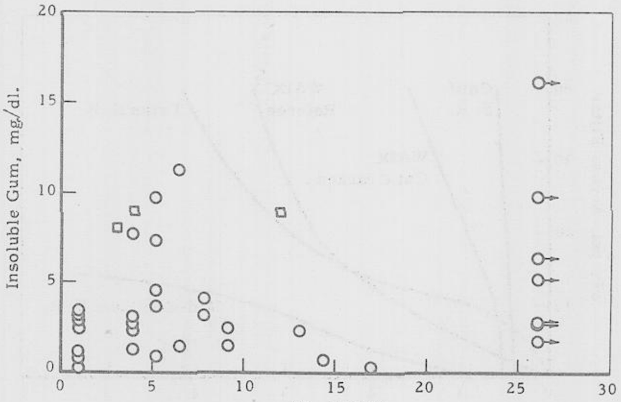

Figure 7. Comparison of insoluble gum and filterability characteristics of desert aged fuels

The behavior of a large number of different fuels is summarized in Figure 7, which plots insoluble gum against the pressure drop observed in the test. The lack of correlation between these two values is readily apparent. The effect of dispersants in the fuel is illustrated by the square points, which represent the behavior of a fuel on aging in the absence and presence of two commercial fuel oil dispersants. The dispersants reduce the filter clogging tendency of the fuel to about one third (*ca.* from 12 to 4) as measured by the pressure drop in the test in spite of the fact they have no effect on the amount of insolubles.

In searching for a reason for the behavior of different fuels the authors examined a number of samples of insolubles with the electron microscope. It became apparent that the filterability behavior was related to the character of the deposit formed. The more crystalline in type the deposit is, the less tendency it has to plug the filter. The deposits could be qualitatively classified into one of four different categories: crystalline, amorphous rigid, amorphous plastic, and diaphanous (Figures 8, 9, and 10). Figure 8 contains an example of crystalline-type material interspersed with some amorphous forms. Figure 9 contains examples of both amorphous rigid and amorphous plastic and suggests that the plastic type is changing over to the crystalline, which may explain the varying behavior of the fuels with time. Figure 10 is a good example of the diaphanous or grape-skin type of deposit; the reason why this fuel rapidly plugs filters is readily apparent. However, in general the interpretation of the pictures is so dependent on the method of sampling and the method of preparing the sample for examination that at the present time there is no sure way of predicting the effect of aging on the filterability characteristics of the fuel. Furthermore, the type of insoluble material formed is not necessarily related to the type of fuel in which it is produced.

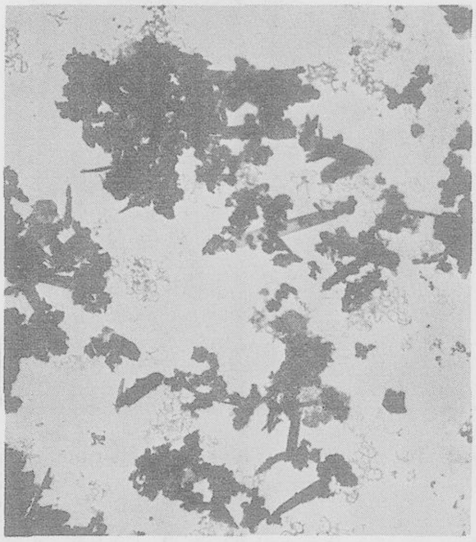

Figure 8. Crystalline and amorphous type insoluble gum from desert aged jet fuel

Another point of considerable interest is the effect of water on filterability characteristics. A great deal of work has been done on this problem both by cooperative work under the egis

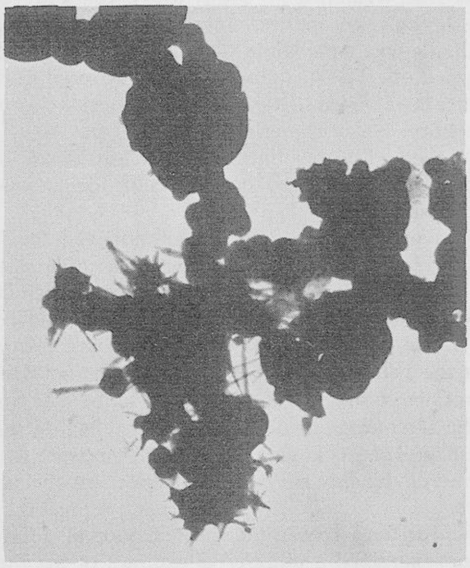

Figure 9. Amorphous type insoluble gum from desert aged jet fuel

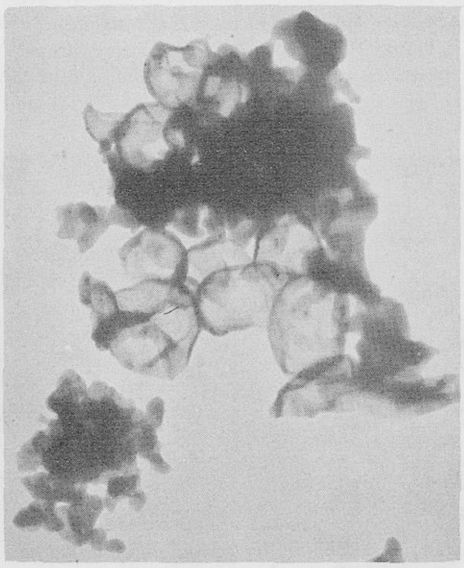

Figure 10. Diaphanous type insoluble gum from desert aged jet fuel

of the Coordinating Research Council and by individual investigators, but it cannot be said that the situation is entirely understood. Figure 11 represents the results of some work with the filterability apparatus mentioned above. Several fuels were tested for filterability characteristics at room temperature and at −22° F. A fuel free of insolubles gave no filterability difficulties at room temperature or −22° F., dry, in equilibrium with 50% humidity air, or saturated with water at room temperature. The failure of the water-saturated fuel to give any filter plugging difficulties may be associated simply with the geometry of the system and is in accord with the sporadic nature of the difficulties arising from ice plugging filters. A more interesting case is that illustrated by the dashed line, which represents a fuel containing 4.0 mg. per dl. of insolubles. Here the filterability difficulties are greatly increased by the presence of insolubles which probably act as nucleation sites for the formation of ice crystals or hydrocarbon hydrates (*1*), which then greatly enhance the filter plugging tendencies of the insolubles. The behavior of the other fuel illustrates the rapid filter plugging which occurs when a fuel is cooled below its freezing point.

HIGH TEMPERATURE STABILITY

In common with many others, the authors have been studying the problem of high temperature stability. Considering the past history of the components, it is surprising that heating a stable straight-run fuel for a few seconds in the neighborhood of 200° to 300° F. leads to the production of sufficient insoluble material to reduce the efficiency of oil-fuel heat exchangers and cause nozzle plugging. The problem is being attacked by examining the behavior of different fuels, pure components, and chromatographic fractions in a laboratory apparatus simulating an aircraft heat exchanger. The laboratory test the authors have used (*4*) is similar to those used by other workers in this field. The test fuel is pumped at 250 p.s.i.g. pressure through a coil of aluminum tubing 1/8 inch in inside diameter and heated by a countercurrent stream of hot air at a rate of 40 ml. per minute (residence time in coil = ca. 22 seconds). The heated fuel (exit temperature, 450° F.) then passes through a 5-micron stainless steel filter, is cooled by another heat exchanger, and finally passes through a pressure regulator. Because constant flow rate is maintained, the pressure differential across the filter is used as a criterion of the degree of plugging. The aluminum coil and the filter are easily removed from the unit for weighing, thus giving a good indication of the rate of deposition of insoluble material.

The test can be operated on either a once-through or recycle basis. Most of the work has been done with recycle, as it has been shown that this is a more severe condition (*5*), and it reduces the amount of fuel required. Under circumstances where plugging is caused by the presence of a very small amount of very active minor components, the recycle method might be less severe. The fuel is refiltered after cooling before being returned to the system.

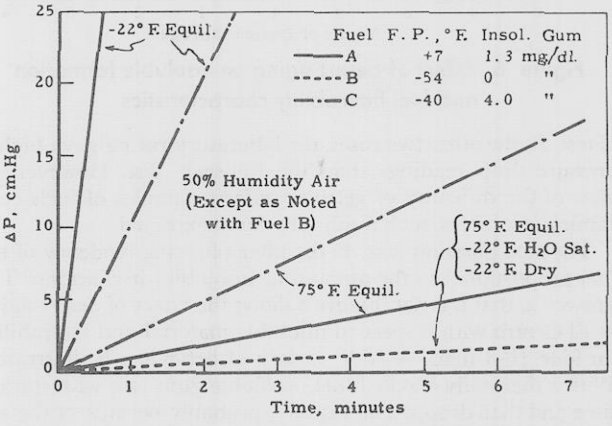

Figure 11. Effect of temperature and water on the filterability characteristics of aged fuels

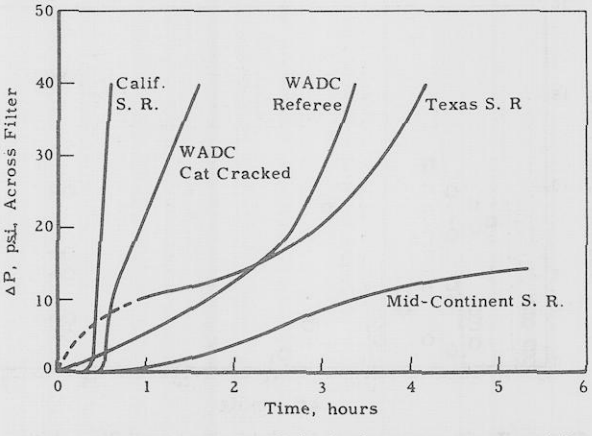

Figure 12. Comparison of the high temperature stability characteristics of several JP-4 fuels

Table I. Properties of Fuels Tested in Laboratory Heat Exchanger Apparatus

Property	California II JP-4 Composite Blend	California II JP-4 S.R. Blend	Texas JP-4 S.R. Blend	Mid-Continent JP-4 S.R. Blend	WADC Referee Fuel	WADC 80% Catalytically Cracked Blend	Solvent A	Solvent B
Gravity, °API	46.6	47.8	53.0	54.5	46.0	45.0	43.9	54.5
ASTM Dist., °F								
IBP	154	136	124	136	130	120	356	358
10%	247	234	220	204	234	197	395	361
50%	331	343	300	288	350	374	428	367
90%	424	410	396	387	448	426	460	381
FBP	504	456	500	482	516	476	476	400
Reid vapor pressure, p.s.i. at 100° F.	2.2	2.5	2.5	3.0	2.7	2.3	1	. . .
Sulfur, wt. %	0.25	0.17	0.087	0.114	0.311	0.101	0.02	0.0015
Nitrogen, wt. %	0.02	0.02	0.002	0.0025	. . .	. . .	0.01 or less	0.005 or less
Br. No., grams/100 grams	28	2.2	0.9	2.3	. . .	43.8	. . .	. . .
Freezing pt. °F.	-76	-80	Below -76	Below -76	-73	Below -76	-40	. . .
Mercaptans, wt. %	0.0028	0.0006	. . . [a]	0.0001	. . . [b]	. . . [b]	. . . [b]	. . . [b]
M.A.V., mg./gram	0.7	. . .	0.3	0.3	. . .	. . .	. . .	. . .
FIA								
Saturates, vol. %	65	86	84	87	72	44	99	95
Olefins, vol. %	12	1	1	1	5	30	0	5
Aromatics, vol. %	23	13	15	12	23	26	1	0
Existent gum, mg./dl.	3	1	3	1	2	3	0	0
Accelerated gum (16 hour), mg./dl.	8	2	9	6	9	54	0	0

[a] Doctor test slightly positive.
[b] Doctor test negative.

The varying behavior of apparently stable, straight-run production JP-4 fuels in the heat exchanger apparatus with recycle operation is illustrated in Figure 12. The properties of the various fuels are given in Table I. While the California JP-4 plugged the 5-micron filter in about 0.5 hour, the fuels from Mid-Continent and Texas sources appeared substantially better with a more gradual rate of pressure increase. The behavior of these fuels in the specification 16-hour accelerated aging test was substantially equivalent. However, one possible clue to the difference in heat exchanger performance may reside in the higher nitrogen and sulfur content of the California fuel. Also shown in Figure 12 are the results obtained on two fuels from Wright Air Development Center both of which contain cracked materials. The blend containing 80% of catalytically cracked components was less stable than the California SR fuel with respect to gum formation during storage, yet it gave somewhat better performance in the heat exchanger test. The referee JP-4 exhibited reasonably good high temperature performance.

Conventional gasoline inhibitors are ineffective in jet fuels for storage stability (*4*); they are also ineffective with respect to high temperature performance. Even the best low temperature jet fuel additive is ineffective in prolonging the filter plugging tendencies of a composite JP-4 fuel, as shown in Figure 13.

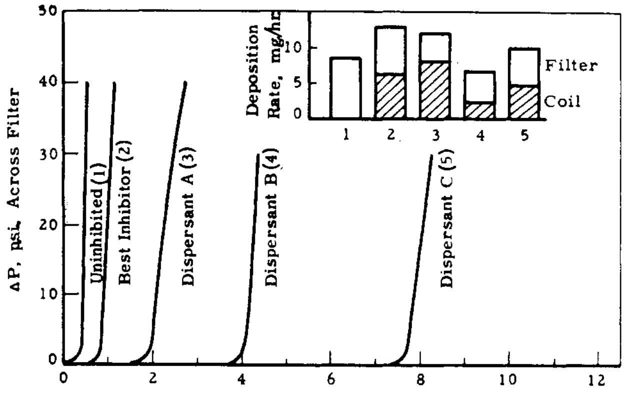

Figure 13. Effect of dispersants on the high temperature stability of a composite JP-4 fuel

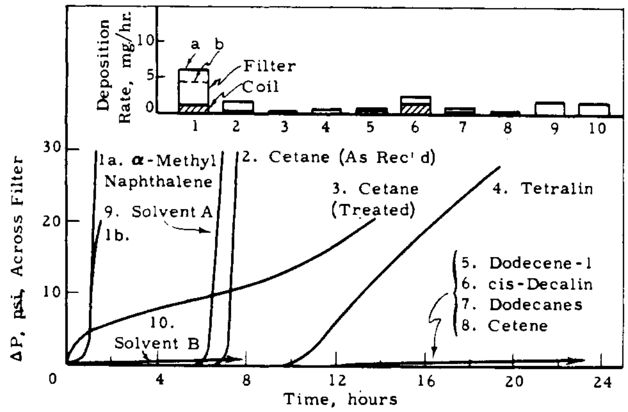

Figure 14. High temperature stability characteristics of various hydrocarbons

Dispersants may offer a better immediate solution, because they can extend the filter plugging time of this fuel by factors ranging from about 4 to 16. However, deleterious side effects with respect to emulsification of water, rust, tank settlings—e.g., sludge— may occur in actual practice. From the bar graphs in the upper right of Figure 13, it may be seen that the dispersants do not reduce the over-all rate of deposition of insoluble residue in the apparatus. (The neat fuel did not operate long enough to form any measurable amount of coil deposit.) Apparently, such additives only increase the ability of the filter to tolerate deposits by modification of the type or size of the particles. The dispersants were of little benefit in reducing the rate of deposition in the coil.

The effects of hydrocarbon type on high temperature deposit formation are also being determined (Figure 14). On the basis of these results, it appears that naphthalene hydrocarbons could be responsible in part, at least, for the instability of jet fuels exposed to severe temperature conditions. Even the deposition rate, as shown by the bar graph (upper portion of Figure 14), approaches that of a jet fuel blend (Figure 13). The result with sample 1a of Figure 14 appeared to be at great variance with CFR fuel coker results reported by Heath and others (*2*). Accordingly, at the authors' request Heath generously donated a sample of his material (sample 1b). It, too, was unstable in the test. This suggests that differences in test design, operating conditions—e.g., residence time, temperature—and filter pore size could have a considerable effect on test results. The coker conditions of 300° F. preheater and 400° F. filter temperatures and 20-micron filter appear considerably milder than the authors' 450° F. exit and 400° F. filter temperatures and 5-micron filter.

The mixed dodecanes performed satisfactorily for over 48 hours without plugging the filter, although appreciable deposit was laid down. A straight-chain paraffin, hexadecane, was less stable, although substantially less deposit and little soluble gum were formed. The dodecanes formed an appreciable amount of soluble gum (*ca.* 15 mg. per dl.), yet considerably less than that by 1-hexadecene and 1-dodecene. These compounds formed a tremendous quantity of steam jet residue (*ca.* 600 and 1000 mg. per dl.) but did not plug the filter during 24 hours of operation. Deposition on the filter was less than that given by the dodecanes. The fact that such quantities of this type of nonvolatile residue can be tolerated suggests that it may not be necessary to use saturated fuels as long as formation of insolubles can be controlled.

Decalin also did not plug the filter during 24 hours of testing, despite the formation of appreciable quantities of coil and filter deposits. Tetralin was less stable than decalin; gradual plugging of the filter started after about 12 hours. Both compounds formed some soluble gum.

For comparison with the various pure hydrocarbons, the results obtained with two straight-run fractions are also included in Figure 14. Solvent A (355° to 475° F.) plugged the filter in about 6.5 hours. Solvent B (360° to 400° F.) operated satisfactorily without plugging for about 7.5 hours. However, this material did not satisfactorily lubricate the pump, thus forcing early termination of the test. The rates of deposit formation of these fractions are low, being more like those of the various hydrocarbons than the JP-4 fuels.

The nature of the deposit formed has been investigated briefly. Analysis of deposits collected from the coil and filter shows that they contain a large proportion of oxygen and some nitrogen and sulfur. They are similar in general composition to the deposit obtained by bomb oxidation at 320° F. for 5 hours under 100 p.s.i.g. oxygen (see Table II). The deposits are black or dark brown, are extremely insoluble in gum solvents, and appear to be fine grained. Figure 15 shows the appearance of a filter before and after a test. It appears that the deposit particles are small enough to have gone through the filter but evidently they are adhesive enough to collect on the surface of the filter.

CONCLUSIONS

There are many problems still to be solved with respect to the stability of turbine fuels. Storage stability, except for saturated fuels, is hardly satisfactory. The relation between the properties of fuels and their filterability after storage has not been solved. The solution to the problem of high temperature stability is only being approached.

Nevertheless, considerable progress has been made on several fronts. The conclusions to be drawn from the present work can be summarized as follows:

Table II. Composition of High Temperature Deposits

	Cumulative Heat Exchanger Deposits		Oxygen Bomb Deposit
	Tube	Filter	
Oxygen, wt. %	14.7	29.5	22.5
Sulfur, wt. %	1.4	. . .	3.6
Nitrogen, wt. %	3.3	. . .	2.1
Carbon, wt. %	70.6	40.8	60.6
Hydrogen, wt. %	4.7	5.3	5.2
C:H ratio	1:0.8	1:1.6	1:1
Acidity, eq./100 grams	0.02	0.25	1.38

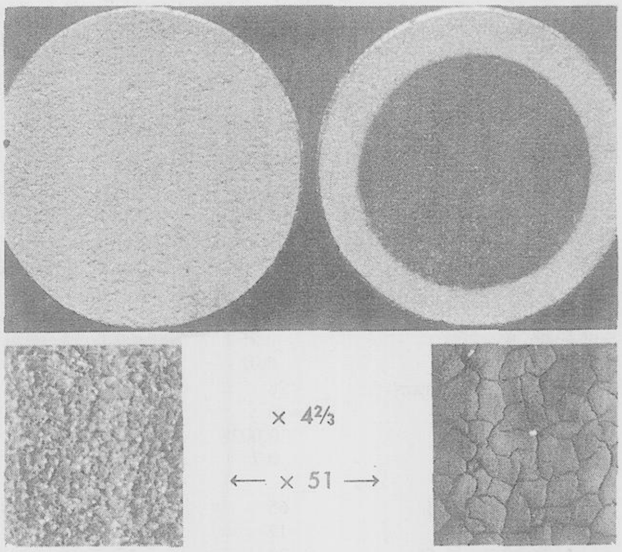

Figure 15. Appearance of 5-micron sintered stainless steel filter before and after laboratory heat exchanger test

The storage stability of jet fuels is a function of their composition—generally decreasing in the order straight-run, catalytically cracked, thermally cracked.

Storage stability can be improved by acid treatment and hydrogenation and by restricting the access of oxygen from the air.

The formation of insoluble gum decreases filterability but not necessarily in proportion to the amount formed.

The effect of insoluble gum on filterability is a function of its microscopic appearance.

The presence of insoluble gum has a particularly deleterious effect on low temperature filterability when water is also present.

Even fuels which appear extremely stable by stability tests cause high temperature deposits.

The rate of filter plugging (ΔP increase) at high temperature can be reduced by the presence of dispersants but the practicability of such a measure has not been established.

Different fuels and pure components vary in behavior with respect to the rate of both filter plugging and deposit formation in both coil and filter. As the rates are not necessarily related, it is obvious that the interrelationship of the character of the deposit and the system in which it forms is very important.

ACKNOWLEDGMENT

Discussions with J. C. Mosteller, R. W. Altman, and O. M. Ballentine of WADC have been most helpful. Assistance by many of the authors' colleagues in these laboratories, particularly by A. M. Cravath, who worked out the technique for and obtained the electron micrographs, and by J. W. Beardmore and R. E. Thorpe is gratefully acknowledged.

LITERATURE CITED

(1) Coordinating Research Council Report of Turbine Low Temperature Pumpability Group, Appendix G, "Colloidal Aspects of Ice Formation, Jet Fuel Filters," F. M. Fowkes, Shell Development Co. Rept. **S-13165**, (October, 1954).
(2) Heath, D. P., Hoffman, C. W., Reynolds, J. H., SAE Meeting, Atlantic City, N. J., June 12–17, 1955.
(3) Johnson, C. R., Fink, D. F., Nixon, A. C., *Ind. Eng. Chem.* **46**, 2166 (1954).
(4) Nixon, A. C., Minor, H. B., *Ibid.*, **48**, 1909 (1956).
(5) Nixon, A. C., Thorpe, R. E., Division of Petroleum Chemistry, 130th Meeting, ACS, Atlantic City, N. J., Sept. 1956.
(6) Schwartz, F. G., Ward, C. C., Smith, H. M., "Studies on the Storage Stability of Distillate Fuels," SAE National Diesel Meeting, Chicago, Ill., Nov. 3–4, 1953.

RECEIVED for review March 28, 1958. Accepted September 8, 1958.
Work done under the sponsorship of the Materials Laboratory, Wright Air Development Center.