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BUREAU OF STANDARDS
WASHINGTON, D. C.

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Oct. 1, 1925.

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Note on Flask Failure in the Oxidation Test

The oxidation test* for mineral lubricating oil consists briefly in heating a 10 gram sample of the oil to be tested in an atmosphere of oxygen for 2 1/2 hours. The number of milligrams of precipitate obtained by diluting the oxidized oil to a volume of 100 cc with light paraffin naphtha is taken as the oxidation number of the oil.

The oxidation flasks are essentially 100 cc erlenmeyer flask bodies with neck about 1/2 inch in diameter and 4 1/2 inches long. The flasks are fitted with nicely ground stoppers.

After the oil is weighed into the flask the air is displaced by oxygen at atmospheric pressure and temperature and the stopper greased and seated, a light spring clamp put on the stopper, and the flask immersed to a point about 1 inch above the base of the neck in a well-stirred oil bath maintained at a temperature of 200°C (392°F). The cover of the bath is about 1 inch above the oil level so that the greased seal and about half of the neck are exposed to room temperature.

It has long been recognized that there is some hazard connected with the presence of oils in high pressure oxygen systems and in view of the possibility of spontaneous ignitions in the oxidation test, although the oxygen is under a pressure of only about 10 pounds per square inch gage, our letter of October 8, 1924, calling attention to this possibility was sent out to users of this test. No cases of flask breakage during the oxidation test as specified have occurred in this laboratory although our experience has included over a thousand tests on several hundred different oils.

Reports have been received during the past two years from four laboratories using the oxidation test, stating that one or more oxidation flasks had burst during the test. These reports have been studied and some experiments made in an attempt to ascertain the probable causes of such occurrences and the possible hazards connected with them. This is a report of the findings to date which, while not conclusive, may be of value to those using the oxidation test.

*Proc. A.S.T.M., Vol. 24, Part II; 1925.

The Oil and Gas Journal, Vol. 24, No. 2, P. 125; 1925.

Mimeographed instruction issued by Bureau of Standards.

The typical case reported is about as follows: A short time, 30 seconds to one or two minutes, after a set of flasks has been placed in the oxidation bath, one of the flasks explodes and at intervals of a few seconds one or more additional flasks may burst. The cover of the bath is displaced and some oil blown out. The extent of the damage reported so far is loss of the flasks, and in one case, minor injury to the operator, due to the splashing of drops of hot oil.

The oxidation flasks are closed with a greased seal and clamp which have been found to release under steady pressures of about 20 pounds per square inch gage. Although with rapidly increasing pressures release will not take place before considerably higher pressures are reached.

Tests on a small number (6) of oxidation flasks indicate that the flasks will burst under hydrostatic pressures ranging from 15 to about 80 pounds per square inch gage. Variations of this magnitude in the behavior of glass are to be expected. The majority of the flasks failed at pressures near 30 pounds per square inch gage.

The pressure developed in the flasks due to heating the gas, oxygen, from room temperature to 200°C is about 10 pounds per square inch above atmospheric and it seems improbable that the vapor pressure of even a very low flash point oil would increase this by more than one pound. It appears then, that both the flasks and the seals have adequate strength for normal operation. It seemed probable that if a flask should burst under a slowly developed pressure of say 20 pounds per square inch, the failure would probably pass unnoticed until the flasks were removed from the bath at the end of the test.

In order to check this point oxidation tests were run with a set of 6 flasks on a light Gulf Coast motor oil diluted with 20% of naphtha recovered from used automobile oils. The resultant mixture had a flash point of 140°F and a fire point of 170°F. Only one flask failed during the test. This failure was a mild pop which did not disturb the bath cover nor cause any interruption to the test although this flask was the nearest to the thermometer and the thermoregulator. The flask failed by the smooth fracture around the bottom which is typical of failure at low pressure. Leakage was observed at the seal of two other flasks indicating a pressure of about 20 pounds per square inch and the low oxidation results from these flasks showed the effect of leakage. The oxidation number of the mixture was about 65. This experiment indicated that failure due to volatile constituents in the oil is not a serious matter.

As stated above, no failures of flasks in the oxidation tests have occurred in this laboratory nor have we yet suc-

ceeded in inducing spontaneous ignitions of the oil in the flasks by the addition of substances, such as metallic oxides, alkalis, etc., to accelerate the rate of oxidation.

During the development work on this test it was observed that often appreciable amounts of water were found in the flasks after they had presumably been given a good opportunity to dry. This water was not evident on casual inspection because of the thin film which water forms on chemically clean glass surfaces, but was detected in the process of weighing the flasks preparatory to weighing in the sample of oil. These occurrences led to the adoption of the practice of allowing the flasks to drain after cleaning, placing them in a drying oven for a half hour, removing and inverting each flask over a suction tube so that air might be drawn into the flask down to the bottom and out through the tube. This procedure ensures dryness and was embodied in the instructions issued for the test.

The recollection of this experience with moisture led to a consideration of the possibility of trouble arising from wet flasks and it was found that a small amount of water, 0.05 gm (1 drop) is sufficient to develop a pressure which will drive a not too tightly fitted cork from the oxidation flask with explosive violence. In these water-oil "explosions" a dense cloud of oil mist and water vapor which resembles smoke is driven from the flask.

Calculations indicated that 0.05 gm of water at 200°C may develop in the flask a pressure of about 15 pounds per square inch absolute which, with the gas and vapor pressure existing, may be above the bursting strength of the flask. The tendency of water drops in oil to superheat and vaporize violently is well known and it is this sudden evolution of vapor which may build up a bursting pressure before the seal can release.

Tests with various amounts of water in the oil showed that with 0.2 cc or more of water in a 10 gram sample of oil the pressure was developed within 40 to 50 seconds; with 0.1 cc, within about 75 seconds; with 0.05 cc, within about 90 seconds; while with 0.025 cc pressures, sufficient to force out the cork were only developed after 3 to 4 minutes. It appears, therefore, that 0.1% of water (0.01 gm) which is more than should be present in a refined oil, will not cause trouble.

Thermocouple observations were then made of the rate of heating of a 10 gm sample of oil in the oxidation flasks when immersed in the oil bath at 200°C. The rate of rise is indicated in the table below. The rate is but little affected by the permissible variations in oxidation flasks, and the elapsed time corresponding to a given temperature may be 10% greater or less than the recorded values as the rate of stirring is very great or very small.

<u>Time Elapsed</u>	<u>Oil Temperature</u>
40 seconds	100°C
78 "	150
110 "	175
240 "	200

These data indicate that the short times reported as elapsing between the placing of flasks in the bath and their failure correspond to oil temperatures of less than 175°C. This is consistent with the observed behavior of oils containing water.

The reported successive failures of two or more flasks of a set at intervals of a few seconds (in one case two different test oils were involved) and the fact that in all cases previous or subsequent tests on the same oils gave no trouble, further support the case for wet flasks because it would be expected that if the failure of the second flask were caused by the first two explosions would be practically simultaneous. Further, since the flasks are usually handled as a set in cleaning and drying it would not be surprising to find that if one flask were wet others of the set which had been handled in the same way would also contain some moisture. The trouble has usually been encountered during the first few tests made in a given laboratory when it is reasonable to expect that the essential requirements for the test had not been fully realized.

Data on the temperature of spontaneous combustion of hydrocarbons in contact with oxygen at atmospheric pressure* indicate that these temperatures are above 250°C for all petroleum products. Lubricating oils, crude oils, and fuel oils ignite at about 260°C and the lighter products, naphthas, etc., at much higher temperatures. This indicates that the temperature of the oxidation test is at least 50°C below the spontaneous ignition temperatures of a variety of petroleum crude oils, fuel oils, and lubricating oils as observed in oxygen at atmospheric pressure and it does not seem probable that the slight increase in pressure in the oxidation flasks would have a great effect in lowering the temperature of spontaneous ignition.

Experiments reported by Dr. Mayo B. Hersey** indicated a spontaneous ignition temperature of about 170°C for lubricating oil in contact with oxygen at high pressure. According to a private communication from him, some later work at pressures below 100 pounds per square inch, showed an increase of ignition temperature with decreasing oxygen pressure sufficient to indicate that there is little probability of spontaneous ignition of lubricating oil in the oxidation test.

*Spontaneous Ignition Temperatures of Liquid Fuels. H. Moore. Automobile Engineer (London) May 1920. P. 199. Ormandy & Craven. Jour. Inst. Pet. Tech. (London); Vol. 10; P. 335; 1924.

**A Study of the Oxygen-Oil Explosion Hazard. Journ. Am. Soc. Naval Eng., Vol. XXXVI, No. 2; May 1924.

In order to gain an idea as to the probable damage which might result from an explosion a number of flasks filled with a mixture of oxygen and gasoline vapor were exploded by electrical means. The results indicated that the damage would be confined to the exploding flask and the splashing of some oil from the bath. If this oil has a fire point well above 200°C (392°F) the probability of ignition of the bath oil appears to be slight.

It is concluded that the available experimental evidence indicates that there is little probability of the spontaneous ignition of lubricating oils in the oxidation test, however, the remote possibility of such an occurrence obviously can not be definitely disproved.

It is also shown that small amounts of water (0.05 gm) which may remain in the flask due to imperfect drying, can generate sufficient pressure to burst the flask. Such failures usually occur within two minutes after placing the flask in the bath. Great care should therefore be taken that the flasks are thoroughly dry.

If explosion should occur it seems that there is little probability of serious damage resulting especially if the bath oil has flash and fire points above the test temperature.

Bureau of Standards,
Washington, D. C.

October 1, 1925.

1870
The first of the year
was a very cold one
and the snow was
very deep. The
frost was very
early and the
wind was very
strong. The
ground was very
frozen and the
trees were very
bare. The
leaves were all
gone and the
branches were
very bare. The
ground was very
frozen and the
trees were very
bare. The
leaves were all
gone and the
branches were
very bare.

The second of the year
was a very warm one
and the snow was
very shallow. The
frost was very
late and the
wind was very
weak. The
ground was very
thawed and the
trees were very
green. The
leaves were all
gone and the
branches were
very bare.

The third of the year
was a very warm one
and the snow was
very shallow. The
frost was very
late and the
wind was very
weak. The
ground was very
thawed and the
trees were very
green. The
leaves were all
gone and the
branches were
very bare.

The fourth of the year
was a very warm one
and the snow was
very shallow. The
frost was very
late and the
wind was very
weak. The
ground was very
thawed and the
trees were very
green. The
leaves were all
gone and the
branches were
very bare.

The fifth of the year
was a very warm one
and the snow was
very shallow. The
frost was very
late and the
wind was very
weak. The
ground was very
thawed and the
trees were very
green. The
leaves were all
gone and the
branches were
very bare.