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THE EFFECT OF ADDED FATTY AND OTHER
OILS UPON THE CARBONIZATION OF
MINERAL LUBRICATING OILS

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THE EFFECT OF ADDED FATTY AND OTHER OILS UPON THE CARBONIZATION OF MINERAL LUBRI- CATING OILS

By C. E. Waters

In a paper on "The Behavior of High-Boiling Mineral Oils on Heating in the Air,"¹ the author called attention to the fact that two straight mineral oils under investigation yielded more "carbonized" matter, insoluble in petroleum ether, when they were heated in brass tubes than when they were heated in glass tubes of the same dimensions. The reverse was true of a third oil having a saponification number indicating the presence of 0.5 per cent of fatty oil. This naturally suggested the advisability of determining the amount of carbonization of a straight mineral oil and of the same oil with known amounts of other constituents, such as lard oil, rosin oil, tallow, etc., added. The results of a series of such determinations are given in the present paper.

The oil selected was an engine oil flashing at 140° in the Pensky-Martens closed-cup apparatus. For the first tests there were seven samples, as follows:

- No. 1.—The straight mineral oil. When 10 g, diluted with 50 cc of petroleum ether, was allowed to stand over night, it yielded only traces of precipitate. These proportions of oil and solvent are the same as those adopted in the carbonization tests.
- No. 2.—The mineral oil heated with Ivory soap shavings for several hours in a closed flask on the steam bath. It was allowed to stand over night and then filtered. After standing several weeks in a closed bottle it set to a sort of jelly, but became perfectly fluid on shaking and remained so. Very little soap was in solution, for it gave only 0.03 per cent of ash.
- No. 3.—The mineral oil saturated with rosin in the same way as with soap. It yielded only 0.03 per cent of matter insoluble in petroleum ether.
- No. 4.—A 10 per cent solution of rosin oil in mineral oil.

¹ Bull., Bureau of Standards, 7, p. 365; 1911. J. Ind. Eng. Chem., 3, p. 233; 1911.
9630°—11

No. 5.—A 10 per cent solution of rapeseed oil in mineral oil.

No. 6.—A 10 per cent solution of lard oil in mineral oil.

No. 7.—A 5 per cent solution of tallow in mineral oil. It yielded 0.20 per cent of matter insoluble in petroleum ether.

As shown in the earlier paper, and confirmed by other determinations to be mentioned later, the insoluble precipitate is an oxidation product. It ought therefore to vary in amount with the time of heating and with the surface of oil exposed to the air. Hence it was first necessary to obtain a set of flasks as nearly alike as possible in internal diameter and in bore of neck. Erlenmeyer flasks of Jena glass were used, and by measuring all that were on hand with a pair of inside calipers made for the purpose, a sufficient number of almost exactly the same dimensions was obtained. Their inside diameter at the widest part was 65 mm, and the bore of the neck 21 mm. They were of 150 cc capacity.

For each determination approximately 10-gram samples were introduced into the flasks, which were then heated to 250° for 5 hours (instead of 3 hours as in our earlier work) in the air bath described in the former paper. The flasks, it may be remembered, were suspended by their necks from openings cut in the cover of the bath, and there was perfect freedom of diffusion of oil vapors and air. After cooling, the flasks were wiped off and weighed to determine the loss by volatilization. Then, after adding 50 cc of petroleum ether, corking and shaking the flasks with a gentle rotary motion until the thick residue went into solution as completely as possible, they were allowed to stand about 22 hours. This length of time seemed to be necessary for complete precipitation and agglomeration of the insoluble matter in a form admitting of easy filtration. If allowed to stand only about 16 hours it was far less manageable.

The insoluble matter was filtered off on Gooch crucibles prepared with a disk of "blue-ribbon" paper (cut with a cork borer), covered with a fairly thick felt of fine asbestos. The residue on the filter was washed with petroleum ether and dried at 93°–95° before weighing. Attempts to dry at the traditional 105°, in some of our earlier work, showed that there was danger of melting the precipitate. The flasks were, of course, thoroughly rinsed

with petroleum ether to remove all oil and precipitate. They were also heated to the same temperature and weighed in order to determine the amount of varnish-like coating on the walls.

During the dry, cold weather, when a large part of the work was done, it was found difficult to entirely avoid static electrical disturbances when weighing. But the errors so caused could not have amounted to more than 2 mg—a negligible quantity in weighing the flasks. The precaution was always taken to touch the balance pan with the finger two or three times in making the final adjustment of the rider.

In making the determinations, four flasks, usually with a different sample in each, were heated at one time. The set of twelve flasks was also used in regular rotation as far as possible. These precautions were taken in order to eliminate accidental variations caused by irregular heating, differences in the dimensions of the flasks, and possible catalytic effects due to the walls of the flasks, as suggested in the first paper.

It may appear to be unnecessary, but for the sake of completeness the flask numbers and the number of each heat are included among the data.

No. 1.—Straight Mineral Oil

Flask No.	1	8	3	10	5	12	3	6	Averages
Heat No.	1	2	4	6	18	9	11	13	
Evaporation loss, per cent.	61.5	47.8	38.8	34.0	34.9	39.5	45.1	51.0
"Varnish," per cent.	0.46	0.35	0.39	0.30	0.12	0.60	0.25	0.20	0.33
Insoluble, per cent.	2.60	2.46	2.07	2.02	1.74	2.65	2.20	2.33	2.26
Total residue, per cent.	3.06	2.81	2.46	2.32	1.86	3.25	2.45	2.53	2.59

No. 2.—Mineral Oil Containing Soap

Flask No.	2	9	4	11	6	5	4	7	Averages
Heat No.	1	3	4	6	18	10	11	13	
Evaporation loss, per cent.	37.1	45.0	43.8	50.9	45.9	42.1	52.8	48.8
"Varnish," per cent.	0.13	0.13	0.14	0.04	0.12	0.05	0.14	0.10	0.11
Insoluble, per cent.	1.96	2.08	1.93	1.92	1.89	1.78	2.61	2.27	2.06
Total residue, per cent.	2.09	2.21	2.07	1.96	2.01	1.83	2.75	2.37	2.17

No. 3.—Mineral Oil Containing Rosin

Flask No.....	3	10	5	12	7	6	9	8	Aver-
Heat No.....	1	3	5	6	18	10	12	13	ages
Evaporation loss, per cent.....	47.1	49.2	40.0	35.1	32.9	51.0	60.2	38.4
"Varnish," per cent.....	0.16	0.19	0.27	0.20	0.46	0.35	0.28	0.27
Insoluble, per cent.....	2.22	2.18	1.96	1.83	2.34	2.72	2.51	2.25	2.25
Total residue, per cent.....	2.38	2.37	2.23	2.03	2.80	3.07	2.53	2.52

No. 4.—Mineral Oil Containing Rosin Oil

Flask No.....	4	11	6	1	8	7	10	1	Aver-
Heat No.....	1	3	5	7	28	10	12	14	ages
Evaporation loss, per cent.....	44.1	47.2	56.1	65.5	41.7	36.7	34.4	43.5
"Varnish," per cent.....	0.34	0.16	0.14	0.40	0.20	0.18	0.07	0.21
Insoluble, per cent.....	1.84	2.02	2.10	2.59	1.79	1.90	1.76	1.19	1.90
Total residue, per cent.....	2.18	2.18	2.24	2.99	1.99	2.08	1.26	2.11

² In heat No. 8 there was some difficulty in regulating the temperature.

No. 5.—Mineral Oil Containing Rapeseed Oil

Flask No.....	5	12	7	2	9	8	11	2	Aver-
Heat No.....	2	3	5	7	9	10	12	14	ages
Evaporation loss, per cent.....	36.4	50.1	48.6	44.6	34.4	43.2	45.1	26.8
"Varnish," per cent.....	1.39	1.35	1.45	1.36	1.55	1.85	0.67	1.37
Insoluble, per cent.....	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.02	0.01
Total residue, per cent.....	1.40	1.36	1.47	1.37	1.57	1.86	0.69	1.38

The reason for the apparently low percentage of "insoluble" and the high percentage of "varnish" is that the flocculent precipitate at first thrown out of the heated oil by the petroleum ether collected, on standing, in small, hard lumps on the bottom of the flask and could not be washed out. No. 6, containing lard oil, showed a tendency in the same direction, but the residue was easily dislodged by a strong stream of petroleum ether from a wash bottle.

No. 6.—Mineral Oil Containing Lard Oil

Flask No.....	6	1	8	3	10	1	12	3	Aver-
Heat No.....	2	4	5	7	9	11	12	14	ages
Evaporation loss, per cent.....	42.0	51.6	52.2	49.2	43.6	49.0	45.2	33.9
"Varnish," per cent.....	0.08	0.03	0.04	0.06	0.24	0.02	0.18	0.09
Insoluble, per cent.....	0.31	0.31	0.33	0.61	0.46	0.32	0.55	0.28	0.40
Total residue, per cent.....	0.39	0.34	0.37	0.67	0.70	0.34	0.46	0.49

No. 7.—Mineral Oil Containing Tallow

Flask No.....	7	2	9	4	11	2	5	4	Aver-
Heat No.....	2	4	6	7	9	11	13	14	ages
Evaporation loss, per cent.....	45.5	38.1	47.9	46.6	41.9	46.8	40.2	35.6
"Varnish," per cent.....	0.10	0.06	0.07	0.05	0.12	0.13	0.09	0.29	0.11
Insoluble, per cent.....	1.35	1.27	1.38	1.47	1.43	1.49	1.25	1.31	1.37
Total residue, per cent.....	1.45	1.33	1.45	1.52	1.55	1.62	1.34	1.60	1.48

The percentages of "insoluble" here given are not corrected for the amount (0.20 per cent) thrown out by petroleum ether before the oil was heated.

A second sample of engine oil, purporting to be the same as No. 1, was obtained, since no more of the latter was available, and it seemed advisable to make some determinations on several mixtures not thought of at first. The descriptions of these new mixtures follow:

No. 8.—New sample of mineral oil.

No. 9.—Mineral oil, to every 10 g of which was added 0.25 g of Syrian asphalt dissolved in 25 cc of xylene. The solution was always added after the oil was weighed, and the solvent driven off by heating on the steam bath, at the same time blowing a gentle current of air into the flask. Before heating, petroleum ether threw out 1.35 per cent of insoluble.

No. 10.—Mineral oil, to every 10 g of which 0.01 g of sulphur dissolved in 1 cc of xylene was added. In this case the solvent was not driven off before heating.

No. 11.—A 10 per cent solution of 55° paraffin in mineral oil. This could be poured about as well as a heavy cylinder oil.

No. 12.—A 10 per cent solution of linseed oil in mineral oil.

No. 13.—Mineral oil and soap. To every 10 g of the oil there was added before heating 0.50 g of finely powdered Ivory soap, dried at 100°–105°.

- No. 14.—Mineral oil oxidized by the combined action of air and sunlight, as described in an earlier paper.³ The oil was placed in a crystallizing dish, in a layer about 1.5 cm deep, covered with a second dish and exposed outside a southern window from February 21 until March 23. Every day or two the oil was thoroughly stirred.
- No. 15.—A mixture of the mineral oil with "Kahlbaum" ferric oxide. In each 10 g of the mixture there was 0.086 g of the oxide.
- No. 16.—Mineral oil oxidized in flasks, but otherwise like No. 14. The oxidation was carried out in this way in order to determine the gain in weight. The average for four flasks, all of which gained nearly the same amount, was 0.92 per cent. This figure represents absorbed oxygen minus carbon dioxide and a little water. The contents of the four flasks were mixed before determining the carbonization. Nearly all of the insoluble oxidation product remained on the walls of the flasks.

The results obtained on heating these oils under the same conditions as for oils 1 to 8 are here given:

No. 8.—Second Sample of Mineral Oil

Flask No.	5	9	7	1(new)	11	1	Aver-
Heat No.	1	2	4	8	9	12	ages
Evaporation loss, per cent.	41.1	34.6	43.6	60.1	49.1	44.0
"Varnish," per cent.	0.22	0.66	0.16	0.49	0.31	0.37	0.35
Insoluble, per cent.	2.08	2.73	1.98	3.18	2.50	2.58	2.51
Total residue, per cent.	2.30	3.39	2.14	3.67	2.81	2.95	2.86

No. 9.—Mineral Oil Containing Asphalt

Flask No.	6	5	8	9	5	2	Aver-
Heat No.	1	4	4	9	10	12	ages
Evaporation loss, per cent.	46.1	51.0	38.3	37.9	30.6	34.4
"Varnish," per cent.	0.31	0.29	0.21	0.22	0.35	0.36	0.29
Insoluble, per cent.	4.95	4.55	4.40	4.55	4.66	4.84	4.66
Total residue, per cent.	5.26	4.84	4.61	4.77	5.01	5.20	4.95

The percentages of insoluble here given are not corrected for the amount thrown out of the oil when petroleum ether is added before heating. As mentioned above, this was 1.35 per cent. The percentages given are figured on the basis of 10 g of oil.

³ Bull., Bureau of Standards, 7, p. 227; 1911. J. Ind. Eng. Chem., 2, p. 451; 1910.

No. 10.—Mineral Oil Containing Sulphur

Flask No.....	7	6	12	10	6	3	Aver- ages
Heat No.....	1	4	5	9	10	12	
Evaporation loss, per cent.....	36.4	65.2	36.0	33.4	37.0	34.7
“Varnish,” per cent.....	0.37	0.54	0.56	0.27	0.19	0.29	0.37
Insoluble, per cent.....	2.81	3.34	2.57	1.89	2.14	2.39	2.52
Total residue, per cent.....	3.18	3.88	3.13	2.16	2.33	2.68	2.89

No. 11.—Mineral Oil Containing Paraffin

Flask No.....	8	4	5	7	1	Aver- ages
Heat No.....	1	3	7	10	11	
Evaporation loss, per cent.....	39.9	42.0	40.8	39.0	39.0
“Varnish,” per cent.....	0.37	0.15	0.15	0.40	0.41	0.30
Insoluble, per cent.....	2.59	2.39	2.33	2.95	3.23	2.70
Total residue, per cent.....	2.96	2.54	2.48	3.35	3.64	3.00

No. 12.—Mineral Oil Containing Linseed Oil

Flask No.....	1	2	6	8	2	Aver- ages
Heat No.....	3	3	7	10	11	
Evaporation loss, per cent.....	50.5	33.0	48.6	36.0	48.1
“Varnish,” per cent.....	6.10	5.29	6.31	6.72	7.09	6.30
Insoluble, per cent.....	0.02	0.03	0.01	0.01	0.01	0.02
Total residue, per cent.....	6.12	5.32	6.32	6.73	7.10	6.32

The petroleum ether threw out a thick, tarry deposit that adhered to the bottom of the flask. This was necessarily counted in with the true “varnish.”

No. 13.—Mineral Oil Containing Soap

The contents of the flasks formed, after heating, a nearly solid cake which could be broken up only with difficulty in petroleum ether. The residue was so fine-grained and gummy that it could not be filtered off.

No. 14.—Mineral Oil Oxidized in Crystallizing Dishes

Flask No.....	9	10	7	4	3	Averages
Heat No.....	5	5	7	8	11	
Evaporation loss, per cent.....	47.7	44.6	42.1	51.6	44.9
"Varnish," per cent.....	0.34	0.30	0.31	0.16	0.26	0.28
Insoluble, per cent.....	5.69	6.06	5.64	5.87	6.76	6.00
Total residue, per cent.....	6.03	6.36	5.95	6.03	7.02	6.28

No. 15.—Mineral Oil Containing Ferric Oxide

Flask No.....	3	11	2	3	4	Averages
Heat No.....	3	5	8	8	11	
Evaporation loss, per cent.....	35.5	51.5	57.1	42.4	44.3
"Varnish," per cent.....	1.11	0.57	1.59	0.60	1.23	1.02
Insoluble, per cent (corr. for Fe ₂ O ₃).....	7.30	4.91	6.58	5.05	8.66	6.50
Total residue, per cent.....	8.41	5.48	8.17	5.65	9.89	7.52

The "insoluble" was corrected for ferric oxide by washing out the Gooch crucible with benzene. With one exception, the weight of the residue was about 2 mg, or 0.02 per cent, greater than the amount of ferric oxide known to be in 10 g of the unheated oil-ferric oxide mixture. Hence the percentages of "insoluble" given above are somewhat too low. The exact amount of the discrepancy must be greater than 0.02 per cent, however, for a small part of the oxide remained in the ring of "varnish" adhering to the walls of the flasks. There were, besides, traces that could not be removed from the bottoms of flasks even with the most careful washing with petroleum ether.

No. 16.—Mineral Oil Oxidized in Flasks

Flask No.....	8	12	4	Averages.
Heat No.....	7	9	12	
Evaporation loss, per cent.....	42.9	40.8	56.0
"Varnish," per cent.....	0.44	0.18	0.31	0.31
Insoluble, per cent.....	7.30	6.12	7.65	7.02
Total residue, per cent.....	7.74	6.30	7.96	7.33

In order to determine whether or not any "varnish" or insoluble is formed in the absence of air, 10-g samples of each of the oils numbered 5, 6, 7, and 8 were heated in flasks with the mouths covered with ground-glass plates. They were heated to 250° for 5 hours. In no case was there any "varnish" formed on the walls, and only traces of insoluble were thrown out by petroleum ether. The loss by evaporation represents in large part the oil which condensed on the glass plates and dripped off or was wiped off the necks of the flasks before they were weighed.

Sample.....	5	6	7	8
Evaporation loss, per cent.....	3.56	5.42	4.64	5.30

DISCUSSION OF RESULTS

In considering the percentages of insoluble obtained on heating any given sample of oil, it is evident that there are causes of variation that may or may not be capable of elimination. A frequent source of annoyance was the sudden changes in the temperature of the air bath. In all of this work two thermometers which gave almost identical readings when heated with their bulbs side by side in an oil bath, were used on opposite sides of the air bath with their bulbs on a level with the oil in the flasks. They were only 8 cm apart, yet would often vary 10° in their readings. Frequently they would be not more than a degree apart for an hour or more, and then one or both would show a change in temperature; or first one and then the other would show a higher reading. The copper bath, with a double bottom and sheathed on the sides with two layers of asbestos with a 3-mm air space between, was heated by a burner with a "rose" top giving a uniformly spreading flame. The flasks were only about a centimeter apart at their widest part and the thermometer bulbs were between opposite pairs of flasks. It seemed, therefore, as if the reactions of cracking and oxidation, which are endothermic and exothermic, respectively, might have something to do with the sudden variations. Evidence of cracking was frequently seen in the sudden evolution of dense fumes from one of the flasks while those next to it were in a comparatively quiescent state. Rarely the fumes ignited spontaneously.

It is also possible that air currents might have caused more or less of the products of combustion from the burner, and hence varying amounts of oxygen, to encircle the necks of the flasks on one side of the bath and thus lower or raise the percentages of insoluble formed. It is hoped to eliminate this possible source of variation and also the irregular heating by means of an electrically heated bath now being made.

The results given in the present paper show, as did those published before, that there is no apparent connection between the amounts of insoluble, evaporation and "varnish."

As to catalytic action, influencing the amount of insoluble, which was hinted at in the earlier paper, a tabulation of the present results fails to give any certain evidence of it.

In the following table are brought together the average values for "varnish," insoluble and total residue for each of the mixtures. There are also given the averages calculated after striking out the most widely variant values, with the exception of those for No. 15, all of which differed so much among themselves that such a recalculation would mean nothing.

TABLE SHOWING AVERAGE RESULTS

Sample	Contains	All values included			Aberrant values omitted		
		"Varnish"	Insolu- ble	Total residue	"Varnish"	Insolu- ble	Total residue
1	Mineral oil	0.33	2.26	2.59	0.32	2.21	2.53
2	Soap	0.11	2.06	2.17	0.13	1.93	2.06
3	Rosin	0.27	2.25	2.52	0.24	2.30	2.54
4	Rosin oil	0.21	1.90	2.11	0.17	1.90	2.07
5	Rapeseed oil	1.37	0.01	1.38	1.42	0.01	1.43
6	Lard oil	0.09	0.40	0.49	0.05	0.31	0.36
7	Tallow	0.11	1.37	1.48	0.09	1.37	1.46
8	Mineral oil (2)	0.35	2.51	2.86	0.35	2.60	2.95
9	Asphalt	0.29	4.66	4.95	0.29	4.66	4.95
10	Sulphur	0.37	2.52	2.89	0.31	2.59	2.90
11	Paraffin	0.30	2.70	3.00	0.39	2.44	2.83
12	Linseed oil	6.30	0.02	6.32	6.38	0.02	6.40
14	Oxidized mineral oil	0.28	6.00	6.28	0.30	5.82	6.12
15	Fe ₂ O ₃	1.02	6.50	7.52	-----	-----	-----
16	Oxidized mineral oil	0.31	7.02	7.33	0.31	7.32	7.63

Comparing the results of Nos. 1 to 7, it is evident that, with the exception of adding rosin, the admixture of other oils to the mineral oil has caused a greater or less diminution in the amount of insoluble and total residue. The same is also true of the "varnish," for as already explained, the apparently high values obtained for No. 5 were caused by the adherence of the insoluble precipitate to the bottom of the flask.

Considering Nos. 8 to 16, we see that the addition of asphalt increases the percentage of insoluble. This is true even if we correct the figures given in the table by the amount precipitated by petroleum ether before the mixture is heated. This is equivalent to 1.35 per cent, calculated on the basis of 10 g of oil.

The addition of sulphur, contrary to expectation, caused no marked difference. The same is true of the addition of paraffin. Linseed oil, as was to be expected, enormously increased the amount of total residue.

The oil which was exposed to the action of sunlight and air in flasks (No. 16) was, presumably, more completely oxidized than that in the crystallizing dish, for it was in a thinner layer, and besides, the flasks were rotated each day so as to spread the oil on the walls. It is not surprising that the figures obtained on heating this oil are higher than those for No. 14.

The results obtained with the mixture containing ferric oxide are interesting, especially in connection with the statement of Worrall and Southcombe,⁴ that the horny or granular deposit at times found in steam cylinders is Fe_2O_3 or Fe_3O_4 cemented together by oil. One would not expect to find much if any rusting inside of the cylinder or carbureter of a gas engine, but it is not impossible that the fine metallic powder resulting from the wearing of the piston and the cylinder walls may become oxidized and then further the carbonization of the lubricant.

CONCLUSIONS

It has been shown that the addition of various oils and other substances to a straight mineral oil affects the amount of carboni-

⁴J. Soc. Chem. Ind., 19, p. 525; 1900.

zation, as measured by the percentage of precipitate thrown out by petroleum ether, in various ways. Lubricants containing soap in quantity (see No. 13), rosin and asphalt, or which have been exposed to the action of sunlight and air, are to be avoided.

One must not conclude, however, from the low results obtained with mixtures containing tallow, lard oil, etc., that the addition of these oils is to be recommended. The presence of the fatty acids resulting from the decomposition of the oils may greatly increase the corrosion of the cylinder and in actual practice cause as much carbonization as the direct addition of ferric oxide would do.

It is intended in the near future to make a series of determinations by heating the above mixtures, and possibly others, with polished strips of iron, brass and other metals.

WASHINGTON, August 24, 1911.

