

## VOLTOLIZATION

Dr. G. W. Nederbragt

Frames 2705-2717

Abstract

This is a series of progress reports by Dr. G. W. Nederbragt of Amsterdam covering the months of July through November, 1942, and March, 1943. The reports give the results of an investigation relating to the manufacture of some finished voltol oils under various conditions with reference to apparatus, current density, etc., and a study of the differences between these voltol oils and Freital finished voltol oil.

The lubricating oils which are manufactured by the polymerization of cracked distillates have, in addition to many favorable properties, the disadvantage that they form carbon in the motor. It is known that the deposition of carbon in the cylinders can be largely prevented by the addition of voltolized rape oil, which keeps the carbon formed in finely divided condition. However, use of voltol oil introduces a new difficulty, namely, the increased tendency of the piston rings to stick. In an investigation of this difficulty by Rhenania, there were indications of a correlation between the tendency of the piston rings to stick and certain properties of the voltolization products.

It was noted in the investigation of various Freital finished voltol oils that the portion of this voltolization product which was insoluble in butenone at 0 C showed fairly large differences in properties, such as consistency, viscosity, etc. This insoluble part consists principally of highly polymerized compounds, which, according to the investigations of Rhenania, are probably directly responsible for the sticking of the piston rings. From the quantity and consistency of this insoluble part, it should be possible to estimate the extent of sticking of the piston rings.

Since it is to be expected that the conditions under which the voltolization is effected will have a great influence upon the homogeneity of the polymerization product, the same raw material which is used in the factory at Freital should be used in the voltolization apparatus in Amsterdam for voltolization under various conditions and for comparison of the properties of the part which is insoluble in butenone with those of the Freital finished oil. Eventually the influence of the apparatus, such as covered or bare electrodes, current density, etc. could be ascertained in this way.

The laboratory voltolization apparatus used in Amsterdam is illustrated in Figure 18,842-A3, Frame 2707. The four voltol tubes, in which the voltolization is effected in the silent gas discharge, are mounted upon a support frame with 90° separations between them and with their axes equidistant from and parallel to the axis of the shaft

about which the frame is rotated in an oil bath. These voltol tubes, of which one is shown in cross-section in the figure, are made of glass. On the inside part a coating of thin copper foil is pressed against the glass, which is connected with the high voltage terminal of a transformer. A second sheet of copper foil is wound on the outside of the voltol tube and grounded through an ammeter. Since the tubes rotate about the central shaft during the voltolization, sliding contacts are necessary for the electrical connections. On the high voltage side, there is only one sliding contact so that the four voltol tubes are maintained at the same voltage; on the low voltage side, there are four sliding contacts so that the current through each of the four tubes can be measured. The current passes through the glass as a displacement current, then as a discharge through the gas and oil, and finally as a displacement current through the second glass wall of the voltol tube. As a result of the rotation of the tubes, the walls are regularly rinsed by the oil subjected to voltolization, which fills each tube about one-third full. Otherwise, over-polymerization would soon occur in places in the tubes. The voltol tubes are connected by means of copper tubes with a hole bored into the axis of the central shaft, to which a suitable sealed rotary connection is made so that the tubes may be evacuated. In this line, a solenoid valve, controlled electrically by means of a mercury filled monometer, which was provided with suitable electrical contacts, permitted control of the pressure in the discharge tubes at any desired value. The oil bath in which the tubes were immersed was provided with suitable temperature control.

A moderate frequency generator, built for 2KVA at 7500 cycles per second, made it possible to pass a discharge of moderate frequency through the voltol tubes, the frequency of which could be varied from 3000 to 9000 cycles per second by regulation of the direct current motor used to drive the generator.

Dr. Nederbragt obtained from Rhenania a rape oil and a mineral oil for the laboratory preparation of finished voltol oil, and also a sample of Freital finished voltol oil with a viscosity of 866 SUS at 212 F for comparison. Later five other samples of rape oil were obtained. From the raw material mentioned first, a small amount of finished voltol oil was made by a process which deviates in various respects from the Freital process. In the apparatus in Amsterdam the electrodes were covered with insulating material, i.e., glass, whereas in Freital the process was operated with bare electrodes. As a result of the higher frequency, 7500 cycles per second (Amsterdam) as contrasted with 500 cycles per second (Freital), a greater current density could be used. Finally, the entire amount of mineral oil was added at once to the semi-voltol oil in the laboratory procedure, whereas it was added in small increments in the Freital manufacturing process. An attempt was made to determine differences between the finished voltol oil prepared by this method of adding the oil and the finished Freital oil by determining the part which is insoluble in methylethylketone

at 0 C, according to the procedure of Rhenania.

The preparation of a small quantity of Amsterdam finished voltol oil, and separation of this product, as well as separation of a finished Freital voltol oil into a part which is soluble and another part which is insoluble in methylethylketone at 0 C was described. Details of the preparation and separation, as well as properties of starting materials, intermediate products, final products, and fractions separated were specified in the report for August, 1942. From these tests, it was concluded that the percentages of the insoluble constituents determined by the separation procedure used were not sufficiently reproducible. The scattering in the results was of the same magnitude as the differences between the Freital and Amsterdam finished voltol oils.

In a subsequent experiment, a larger quantity of Amsterdam finished voltol oil was prepared and a new separation with methylethylketone at 0 C in triplicate gave a satisfactory result after suitable modification of the procedure. Details of this preparation and separation, and the percentages and properties of various fractions separated from the Freital and Amsterdam finished voltol oils are specified in the report for September, 1942. From these results, it was concluded that the percentage which is insoluble in methylethylketone differs significantly for Freital and Amsterdam finished voltol oils, amounting to 23.0 per cent by weight for the former and 34.4 per cent by weight for the latter. Also, the product in both cases had different properties: the insoluble part of the Amsterdam voltol oil was viscous and ropy, whereas that of the Freital finished voltol oil was more gumlike. According to the experience of Rhenania, as Professor Zerbe indicated, this difference accompanies a different behavior in experiments on sticking of the piston rings: the gummy product had a greater tendency to cause sticking. The manufacturing procedure used was different in the following respects: bare electrodes were used in Freital whereas glass covered electrodes were used in Amsterdam; secondly, a lower frequency and current density was used in Freital than in Amsterdam; and finally, in Freital the mineral oil was added in small increments to the semi-voltol oil during the final voltolization, whereas in Amsterdam, all the mineral oil was added at once to the semi-voltol oil prior to the final voltolization. It remains to be determined which of these factors causes the difference between the Freital and Amsterdam voltol oils.

The portions of the Freital as well as the Amsterdam finished voltol oils which were insoluble in methylethylketone and which were obtained in the extractions in triplicate were combined and served as material for the molecular weight determination, elementary analysis, and determination of the specific refraction. These determinations were made by Dr. J. J. Leendertse. The molecular weight determinations were made by the boiling point method, using benzene as well as methylethylketone as the solvent. Because of the practically complete insolubility of the Freital product in both solvents, even with prolonged heating, it was not possible to determine the molecular weight of this material. The solubility of the Amsterdam product in both solvents was greater. However, with methylethylketone the molecular weight

determination was not very satisfactory because of the rather low solubility of the Amsterdam product in the solvent, and because of the excessive tendency of the solvent to foam and superheat. Therefore, from this determination it could only be stated that the molecular weight is of the order of magnitude of 2000 to 5000. With the use of benzene as the solvent, similar difficulties were encountered, although to a much smaller degree; 2000 to 3000 was found for the molecular weight with it. The specific refraction of the insoluble extraction product of the Freital finished voltol oil was not determined because of the difficulty of determining the specific weight of this product. The results obtained for these methylethylketone-insoluble fractions are:

|   | <u>Freital Finished<br/>Voltol Oil</u> | <u>Amsterdam Finished<br/>Voltol Oil</u> |
|---|--|--|
| $n_D^{20}$                                  | 1.4905                                 | 1.4955                                   |
| $d_4^{20}$                                  | -                                      | 0.9391                                   |
| $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$ | -                                      | 0.3109                                   |

The elementary analyses were made in an apparatus for use with sulfur- and nitrogen-free products. A preliminary determination of the sulfur content of both products indicated a sulfur content of 0.14 per cent in the Freital product and 0.11 per cent in the Amsterdam product. The results of the elementary analyses are as follows:

|               | <u>Freital Product</u> | <u>Amsterdam Product</u> |
|---------------|------------------------|--------------------------|
| C             | 79.89 - 79.77          | 80.76 - 80.87            |
| H             | 12.03 - 12.03          | 12.07 - 12.06            |
| 100 - (C + H) | 8.08 - 8.20            | 7.17 - 7.07              |

In the product from the Amsterdam finished voltol oil there is less oxygen, which may explain a stronger copolymerization with the mineral oil. This stronger copolymerization of the mineral oil may possibly be explained by the fact that in the preparation of the Amsterdam finished voltol oil all the mineral oil was added at once to the semi-voltol oil. Plans were made to examine this point by comparison of Freital and Amsterdam finished voltol oils, which were to be prepared by mixing the rape oil and mineral oil before effecting the voltolization, and not adding any mineral oil during the voltolization as was previously done. An Amsterdam finished voltol oil was subsequently prepared in this way and extracted with methylethylketone. Arrangements were made with Professor Zerbe of Rhenania to produce a comparable oil at the plant at Freital from the same base stocks, which were to be mixed before the voltolization was started.

According to the subsequent report, this modified Freital finished voltol oil was never received from Professor Berbe.

The different finished voltol oils were compared with respect to their sludge supporting effect. It was first attempted to use Shell carbon black as sludge. However, the rate of settling of Shell carbon black in double or triple Shell lubricating oil was not significantly influenced by the addition of finished voltol oil. Subsequently, a sludge obtained by centrifuging used motor oil was used instead of the carbon black. This sludge was added to triple Shell or mixtures of single Shell or double Shell lubricating oils containing finished voltol oil, which were selected in such a way that they had the same viscosity as triple Shell lubricating oil at 50 C. The sludge content of a sample of each mixture was determined immediately after addition of the sludge. Samples of 50 cc of each in graduated cylinders were then placed in a thermostat at 50 C. After 48 hours, the sludge content of the upper 10 cc from each graduate was determined. This sludge content was determined by filtering the oil through filter paper, washing the paper with naphtha, and finally weighing, each determination being made in duplicate. The results of these determinations are tabulated in the report for March, 1933. It was determined that the sludge supporting effects of the Freital and Amsterdam finished voltol oils were approximately equal; that of a sample of the Amsterdam finished voltol oil, prepared by adding the mineral oil to the rape oil before voltolization, was nearly as great.

It was stated that the electrical energy expended and the length of time required for the preparation was greater if the mineral oil was added to the rape oil before voltolization than was the case when mineral oil was added to the rape oil in increments during the course of the voltolization.

It was not determined whether the less gummy insoluble part of the finished voltol oil really caused decreased sticking of the piston rings, as was assumed by Kinnear. Future work was planned but not reported.