DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS
OF THE
BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 86

**RESISTANCE OF AN OIL TO
EMULSIFICATION**

BY

WINSLOW H. HERSCHEL, Assistant Physicist
Bureau of Standards

ISSUED FEBRUARY 17, 1917

WASHINGTON
GOVERNMENT PRINTING OFFICE
1917

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By Winslow H. Herschel

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I. INTRODUCTION

1. FORCED-FEED LUBRICATION

Lubricating oils are used to reduce friction, and their effectiveness depends upon the manner in which they are applied as well as upon their quality. To obtain the best results there must be

an abundant supply of the lubricant.¹ It has thus become recognized as good practice, especially for high-speed machinery, to use a forced-feed lubricating system, the oil being pumped from a settling tank through the bearings and allowed to flow back to the tank. A filter is included in the circuit.

It has been found that oils do not wear out mechanically and may be used over and over again. Thurston² says, "A mineral oil is usually just as good after use as before, apart from the impurities, which are removed by filtering." Similarly, Sabatié and Pellet³ conclude, "The apparent result of all these different tests is that a used oil, received in good condition and *filtered with care* [their italics] to rid it of the material which it may contain in suspension, preserves its different properties almost intact."

It is to be regretted that the authors do not always state the length of time their oils had been subjected to use. In the one case where the time is given a motor was run for eight hours, and probably the other runs were of short duration. The tests, therefore, throw no light on the question of the gradual breaking down of an oil due to chemical changes when it is in use for months or years without complete renewal.

2. NEED OF TEST FOR EMULSIFICATION

The subject of emulsification is of greatest importance in connection with high-speed engines and steam turbines. More or less water is sure to find its way into the oil from leaky stuffing boxes or cooling coils, and thus all the conditions are present for the formation of an emulsion of oil and water.

It is on account of the necessity for filtering, upon which emphasis has been laid, that an emulsifying oil can not be used in a circulatory system. An emulsion may clog the filter and result in damage to the bearings, due to failure of the oil supply. Both on account of this danger and the length of time required for a service test it is of great practical value to have a laboratory test by which it may be determined whether an oil will emulsify in use.

In devising such a test the following requirements have been kept in mind:

1. The apparatus should be reproducible and readily constructed and made use of by any operating engineer.

¹ See B. Tower, Proc. Inst. M. E., p. 632, Table X; November, 1883.

² R. H. Thurston, A Treatise on Friction and Lost Work in Machinery and Millwork, p. 380; 1903.

³ Bulletin du Laboratoire d'essais, No. 16, 1911; Essais d'huiles usagées, P. Sabatié and M. Pellet.

2. The test should require the minimum amount of time and material consistent with the required degree of accuracy.

3. The resistance to emulsification should be expressible by a single numerical value, ranging from a minimum reached by but few of the worst oils to a maximum attained by only a few of the best.

It is not necessary for an operating engineer to determine the cause of emulsification, since an emulsion is undesirable whether due to soap, fatty oils, or other components. Fatty oils would probably not be used as adulterants, since they are more expensive than mineral oils, but any possible discrimination against them may be avoided by applying the test only to supposedly nonemulsifying, pure mineral oils.

3. TESTS PREVIOUSLY DESCRIBED

The few tests which have been described in print are, almost without exception, very indefinite. Archbutt and Deeley⁴ give the following:

Emulsification Test.—Oils used for forced lubrication should separate quickly and completely from water. To test this property, equal volumes (say 50 cc each) of the oil and water should be heated to 80° C or 180° F and vigorously shaken together for 10 minutes in a corked bottle about 2 inches internal diameter. Some mineral oils will, on allowing the bottle to stand, separate from the water rapidly and completely, others will form an emulsion which breaks up quite slowly.

It is evident that "vigorously" is a relative term which requires exact definition. In Bryan's⁵ description of his test the method of agitation is hardly more exact. Speaking of mixtures of half water and half oil, he says:

These mixtures were stirred in a pint commercial fruit jar for five minutes, and were then poured in graduated glass cylinders and allowed to settle out at room temperature (70° to 80° F), observations being made periodically of the total amount of oil and water that had not separated from the mixture.

Bancroft⁶ has compiled a great amount of information about emulsions, but there is comparatively little which is applicable to the present problem because the experimenters quoted were dealing mainly with fixed oils and permanent emulsions. Pickering,⁷ Ostwald,⁸ Lewis,⁹ Ellis,¹⁰ and Donnan and Potts,¹¹ however, experi-

⁴ L. Archbutt and R. M. Deeley, *Lubrication and Lubricants*, p. 343.

⁵ G. S. Bryan, *Journal Am. Soc. Naval Engrs.*, 26, p. 559; 1914.

⁶ W. D. Bancroft, *Journal of Physical Chemistry*, pp. 177, 345, 475, 739, 1912; p. 501, 1913.

⁷ S. U. Pickering, *Trans. Chem. Soc. London*, 91, Part II, p. 2001, 1907; *Zeit. Kolloidchemie*, 7, p. 11, 1910.

⁸ W. Ostwald, *Zeit. Kolloidchemie*, 6, p. 103; 1911.

⁹ W. C. McC. Lewis, *Zeit. Kolloidchemie*, 4, p. 211; 1909.

¹⁰ R. Ellis, *Zeit. Phys. Chem.*, 78, p. 321; 1911.

¹¹ F. G. Donnan and H. E. Potts, *Zeit. Kolloidchemie*, 7, p. 208, II; 1910.

mented with mineral oils. The last two experimenters used a "specially constructed shaking machine," which would probably be difficult to reproduce and, at any rate, is not described. Lewis speaks of "48 hours' vigorous shaking." Ellis says, "A special, acid-free cylinder oil was shaken with distilled water, free from carbon dioxide, in steamed-out Jena glass flasks. After shaking for two or three days, etc." Pickering remarks, "It is possible to judge immediately by the working of the syringe whether it [emulsification] has occurred or not; but when it has not occurred no continuance of the pumping, without altering other conditions, will produce emulsification."

A consideration of these various methods led to the conclusion that none of them was suitable for the purpose at hand and that a reproducible test could best be based on the stirring machine used by Bryan. Consideration was also given to the method of emulsifying in common use by chemists¹² of passing steam over or through the oil, but it appeared too indefinite unless a determination were made of the quantity and quality of the steam. These measurements would be difficult to make, and in fact are not attempted by those who use this method of agitation.

II. PROPOSED APPARATUS AND METHOD

The general form of the apparatus and the method of procedure finally adopted will be briefly indicated, and then a somewhat detailed consideration will be given to the various items of design and method of use.

1. APPARATUS

A general view of one form of the apparatus is shown in Fig. 1. The oil to be tested, with double its volume of water, is placed in the graduated glass cylinder. A flat metal paddle, carried on a vertical shaft, is rotated by an electric motor. The speed is indicated by a liquid tachometer attached to the upper end of the motor shaft, and speed control is obtained by means of a sliding rheostat. The paddle shaft, of course, might be driven by hand, but the motor drive is much more convenient.

The glass cylinder is placed in a bath, consisting of a brass cup filled with water, and the bath is brought to the desired temperature by means of a Bunsen burner. One feature of the apparatus, not evident from Fig. 1, is a false bottom to the bath, permitting a circulation of water below the cylinder. It is possible that this

¹² G. S. Bryan, *loc. cit.*, p. 561; P. H. Conradson, *Journal of Industrial and Engineering Chemistry*, p. 171, May, 1910; *Proceedings American Society for Testing Materials*, 16, Part II, p. 273, 1916.

could be dispensed with without danger of breakage of cylinders from temperature changes.

It would be an advantage to have the water bath large enough to hold, say, half a dozen cylinders, so that no time would be lost in waiting for the liquids in the cylinders to reach the temperature of the bath. The same saving of time could be obtained, of course, by using a separate bath, unconnected with the stirrer, or using hot water, from any other source, to mix with the oil in the cylinders.

2. DEFINITION OF DEMULSIBILITY

Since it is impossible at present to express resistance to emulsification in cgs or other rational units, the method selected must be wholly arbitrary. Two general methods may be imagined. Either oils could be emulsified to a constant degree, the variable intensity of the agitation required serving as a measure of the resistance, or the oils could be agitated with the same violence and the resisting power measured by the extent to which they emulsified. I have adopted the second method and taken the rate of separation of the oil from the emulsion as a measure of the effect produced by the stirring. The word "emulsion" is used to signify any mixture of oil and water without implying thereby that all such mixtures are true emulsions. While I regard it as probable that rapidity of separation is an indication of high resistance to emulsification, I can offer no rigid proof in support of this point of view. Yet even if it were possible to imagine an oil which would emulsify easily and still settle out rapidly from an emulsion, it would be justifiable to take the rate of settling as a criterion for the particular quality of the lubricant which is to be measured. For what is required is an oil which will de-emulsify between the time it passes through the bearing and the time it reaches the filter on its next journey around the circuit.

When an emulsion of oil and water is allowed to stand in a cylindrical glass vessel, there will usually appear, sooner or later, a fairly clear meniscus between the emulsion and a layer, above it, of oil which has separated out, and this meniscus will fall as the layer of oil increases in depth. Meanwhile a second less distinct meniscus, separating the emulsion from the water below it, will work its way up from the bottom of the vessel. When it was found that, with the methods of agitation employed, some oils separated completely from the water in one minute or less, it became evident that the extent to which the oil had emulsified could not be measured by the size of globules, viscosity, or other

physical characteristics of the emulsion unless more effective means of agitation were devised. Neither could observations be made of the amount of emulsion remaining after a given time of settling, the method used by Bryan and also by Conradson. Experience has shown that this procedure is objectionable because it necessitates reading the lower meniscus, which is often very indistinct and indefinite, the emulsion forming a honeycomb filled with water. A slight jarring of the vessel will then cause the lower meniscus to rise considerably, so that its location has little significance.

Bryan and Ostwald both observed the volumes of oil and water which settled out of the emulsion after different intervals of time, and found that the rate of settling is not constant. Table 1 shows readings obtained from a certain oil, using a cylinder graduated from the bottom and containing 60 cc of emulsion. The oil which settles out is often cloudy and is, in fact, an emulsion containing a small amount of water. It should be noted that the rate of settling, as given in the last column, is always the average rate between the time of stopping the paddle and the time of observation and not the rate between two successive times of observation. The maximum rate is here 112, and this is taken as the measure of the resistance of the oil to emulsification. There would be some objection to saying that the emulsibility of this oil was 112, because a high tendency to emulsify would then be represented by a low number. Philip's ¹³ term, "demulsification value," suggested the word "demulsibility," meaning resistance to emulsification or tendency to de-emulsify, and this name has been adopted for the highest rate of settling, found as in Table 1. Thus a high demulsibility indicates a high resistance to emulsification.

TABLE 1
Rate of Settling of Oil from an Emulsion with Water

Time since stopping paddle	Reading of cylinder at upper meniscus	Oil settled out, = 60— column 2	Rate of settling per hour
	cc	cc	cc
5 minutes.....	52	8	96
6 minutes.....	50	10	100
7 minutes.....	47	13	112
8 minutes.....	45	15	112
9 minutes.....	44	16	107

¹³ Arnold Philip, *Journal of the Society of Chemical Industry*, p. 697; July 15, 1915.

The term "demulsibility" therefore may be defined as the maximum rate of settling out of an oil from an emulsion, in cubic centimeters per hour, when the emulsion is made and the rate of settling is found as follows:

Twenty cubic centimeters of oil and 40 cc of distilled water are placed in a 100 cc cylinder having an inside diameter of 26 mm and heated in a water bath to 55° C. The liquids are then stirred with a paddle for five minutes at a speed of 1500 r. p. m. The paddle is simply a metal plate 89 by 20 by 1.5 mm submerged in the liquid. The cylinder is allowed to stand for a time not exceeding one hour at a temperature of 55° C, and from each of the readings, taken as frequently as necessary, of the volume of oil settled out from the emulsion, there is calculated the average rate of settling between the time of stopping the paddle and the time of observation. The maximum rate of settling, thus obtained, is called the demulsibility, and is used as a measure of the resistance of the oil to emulsification. The maximum possible demulsibility is 1200, as the first reading is taken one minute after stopping the paddle.

3. PADDLE

Any stirrer similar to a screw propeller or of other complicated shape, would be difficult to describe or to reproduce. If it were not for this restriction, a mechanical egg beater, found in most households, might have been adopted, as it is an efficient emulsifier. For the sake of simplicity it was decided to use a rectangular plate which could be completely described by its length, breadth, and thickness. When the test was first reported to a committee of the American Society for Testing Materials,¹⁴ March 5, 1915, the dimensions recommended were $3\frac{1}{2}$ by $\frac{7}{8}$ by $\frac{1}{32}$ inches. This size of paddle resulted from the provisional adoption of 60 cc of liquid (oil and water together) stirred in a 100 cc cylinder having an inside diameter of 1 inch. With this volume of liquid, filling the cylinder to the height of about 105 mm ($4\frac{1}{8}$ inches), as approximately the maximum amount which could be used without spilling, and with the necessity of keeping the paddle submerged so that the formation of foam should be avoided as much as possible, it appeared that 89 mm ($3\frac{1}{2}$ inches) would be the maximum length that could be used. The width of 22 mm ($\frac{7}{8}$ inch) resulted from the assumption that a narrow clearance between the edge of the paddle and the cylinder walls was necessary to produce the emulsifying effect,

¹⁴ A preliminary account appeared in *Proceedings A. S. T. M.*, 16, Part II, page 248; 1916.
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and that 2 mm ($\frac{1}{16}$ inch) was the narrowest clearance which could be conveniently used.

Subsequently, a series of copper paddles were prepared, having approximately the dimensions given in Table 2 in order to find the influence upon the emulsifying effect of varying the paddle dimensions.

TABLE 2
Dimensions of Paddles

Paddle	Length		Width		Thickness	
	Inches	Milli-meters	Inches	Milli-meters	Inches	Milli-meters
No. 1.....	3½	89	$\frac{7}{8}$	22	0.03	1.0
No. 2.....	3	76	$\frac{7}{8}$	22	.03	1.0
No. 3.....	2½	64	$\frac{7}{8}$	22	.03	1.0
No. 4.....	3½	89	1½	24	.03	1.0
No. 5.....	3½	89	1½	20	.03	1.0
No. 6.....	3½	89	$\frac{7}{8}$	22	.05	1.5
No. 7.....	3½	89	$\frac{7}{8}$	22	.07	2.0

After these paddles had been tried with three oils of different quality, and it was found that the rate of settling, which was used as a measure of the emulsifying effect, was the same with all paddles, so long as the oil was not changed, paddle No. 5 was cut down to a width of 15 mm and No. 4 was cut to a width of 10 mm. Only in the case of the 10 mm paddle was the observed rate of settling appreciably different than before.

It had been found that paddle No. 1 was apt to become bent when vigorously wiped, and though this difficulty might have been reduced by making the paddle of steel the use of a thicker paddle offered an equally simple remedy. It also seemed advisable to decrease the width of the paddle so as to obtain a wider clearance, both on account of possible irregularities in the cylinders and defects in the automatic holding device which might be devised. In view of these considerations and of the fact that changes could be made in the paddle dimensions without changing the rate of settling, it was decided to adopt a width of 20 mm and a thickness of 1.5 mm, leaving the length 89 mm, as in paddle No. 1.

4. OIL CONTAINER

In order to avoid the drainage losses which are unavoidable when the emulsion is poured from one vessel to another, as in Bryan's test, it appeared preferable to stir the oil and water in the

graduated cylinder itself, so that the only possible drainage loss would be that due to the emulsion clinging to the paddle when it was withdrawn, a loss which could be reduced to a negligible amount by wiping the paddle with the finger and returning to the cylinder the emulsion thus collected. The article by Philip,¹⁵ which appeared subsequently, confirmed the desirability of avoiding drainage losses. He says: "One of the results of the drainage losses in transference is that even an ideal oil can not give a demulsification value greater than about 98 per cent," demulsification value being defined as the ratio of volume of oil separated out from an emulsion after standing 24 hours to the total volume used.

In deciding upon a 100 cc cylinder, the following considerations were kept in mind:

1. The amount of oil required should not be large.
2. The total amount of oil and water should not be large enough to overflow when stirred at high speed.
3. The cylinder should be a readily obtained commercial article.

The specifications under which 100 cc graduated cylinders are purchased by the Government departments are equivalent to allowing a permissible variation of inside diameter of from 27.4 to 25.9 mm, and the tests with varying clearance, using the paddles given in Table 2, indicate that this variation in diameter would have no effect.

Experience has shown that the danger of breaking the cylinder in making the test is very slight. In the apparatus in use at the Bureau the cylinder is held by hand, but it is believed that an automatic holder could be devised with the use of which breakage would be equally negligible and which would require a less careful operator.

5. TEMPERATURE

Bryan recognized that both the temperature at which the oil and water were mixed and that of the emulsion while settling affected the results, but he did not adopt any standard temperature. The choice of a temperature is somewhat arbitrary, but by using 55° C (130° F) the following advantages are obtained:

1. There is no danger of breaking the cylinders from sudden changes of temperature.
2. The temperature can always be reached by heating the cylinders in a water bath by means of a Bunsen burner. The use of ice, which is much less convenient to manipulate, is avoided.

¹⁵ Arnold Philip, loc. cit., p. 700.

3. The test is made at approximately the average running temperature of journal bearings.

4. 130° F is one of the standard temperatures for viscosity determinations recommended by a committee of the American Society for Testing Materials.¹⁶

Fig. 2 shows the effect of varying the temperature of the bath for four different oils. In these and all other tests which are to

FIG. 2.—Effect of temperature upon rate of settling

be reported the emulsions were allowed to settle at the same temperature as that at which they had been stirred. The speed was 1500 r. p. m. for five minutes, except for the lowest curve, where the speed was 900 r. p. m. In all tests (also those shown in Figs. 3 and 4) the emulsion was made from 20 cc of oil and 40 cc of water.

¹⁶ Proceedings, Part I, p. 280; 1915.

6. DURATION

Bryan and Philip continued the agitation of the liquid for five minutes. Bancroft¹⁷ gives the point of view of the pharmacist as follows:

Five minutes of very rapid trituration will accomplish more in emulsifying an oil or balsam than an hour of slow trituration. Indeed, if after five minutes or less of rapid trituration an oil does not emulsify, it is good evidence of some fault in the ingredients used or of their proportions, and a satisfactory emulsion can not be expected without alteration of the ingredients.

It should be remembered in reading the above that for the purposes of the pharmacist a "satisfactory" emulsion must be a permanent one.

Fig. 3 shows the effect of changes in the duration of stirring for three different oils, the speed being in all cases 1500 r. p. m. In these tests (also those shown in Figs. 4 and 5) the temperature used was 50° C (122° F), this having been tentatively adopted as standard. Since no marked decrease in the rate of settling could be obtained by prolonging the stirring beyond five minutes, and as a duration of approximately this length was desirable in order that errors in starting, stopping, and adjusting the speed of the paddle should be negligible, five minutes was adopted as standard.

7. SPEED

No precedent could be found for any particular speed, although the quotation from Bancroft indicates that a high speed is desirable. Bryan turned his stirrer by hand. Ostwald¹⁸ used an electric motor, but his paddle had an up-and-down motion like a churn, and his speed is not stated:

The tests were made by pouring the two liquids to be emulsified into a graduated cylinder and agitating them with constant velocity for a given length of time (mostly five minutes) with the help of a glass paddle and an electrically driven shaking machine suited to the purpose. With a suitable construction of the paddle, suitable stroke, and a suitable velocity found by trial, in this way a snow-white emulsion was obtained out of, for example, kerosene and water, which began to clear at the top and bottom after standing. In general, with clean test conditions, two quite sharp menisci were to be seen, whose position on the cylinder divisions were read off and plotted on coordinate paper against time intervals.

A perfectly nonemulsifying oil would show a rate of settling of 1200 cc per hour, no matter what the speed of paddle, and it would naturally be expected that with any oil of inferior quality the rate of settling would decrease with the speed. If this were

¹⁷ Loc. cit., p. 756, Quoted from Scoville, *The Art of Compounding*, 81; 1895.

¹⁸ Loc. cit., p. 106.

so, the higher the speed the more marked would be the difference in the rate of settling of different oils. Fig. 4 shows that this supposition is only partially true, for in general there is a speed

FIG. 3.—Effect of duration of stirring upon rate of settling

above which the rate of settling increases, as for oils A and B. This limiting speed does not appear to have been reached for oils C and E. Oil D showed at times the adhering drops (which will

be discussed later) and the concomitant increase in the rate of settling whenever the speed reached 1800 r. p. m. or over. In all tests of Fig. 4 the stirring was continued for five minutes, as also

FIG. 4.—Effect of speed of paddle upon rate of settling

in tests of Fig. 5. On the whole, it appeared that a speed of 1500 r. p. m. would give, on the average, a minimum rate of settling. This speed has the advantage of being high enough so that the paddle can be direct connected to an electric motor.

8. TACHOMETER

The liquid tachometer, which is shown in Fig. 1 above the motor, has the advantages of noiselessness, durability, and reliability on account of there being no parts to wear out nor belt to slip. Any liquid, such as an oil, may be used which does not evaporate readily and which gives a clear meniscus, and the readings are independent of the density or of the viscosity of the liquid. When the motor is still, the liquid should stand at the zero line, it being necessary to add or withdraw a little oil at infrequent intervals on account of variations in the volume of oil with the temperature. This slight trouble could be avoided by the use of a sliding scale, but it is simpler to etch the scale on the glass tube or paste on a strip of paper, the scale and meniscus both being clearly visible when the motor is running. The distance which the meniscus will rise or fall from the zero line when the motor is started may be calculated from the formula

$$h = d = \frac{(0.1047 \, n)^2}{4g} R^2,$$

where h is the height of the edge of the meniscus above the zero line and d the depth of the center of the parabolic surface below the line for a speed of n revolutions per minute. R is the inside radius of the glass tube, and $g = 980.7$ cm per sec.² (32.17 feet per sec.²). In graduating the scale it is convenient to find the depression, d , when the motor is running at nearly its maximum speed, by inserting a hand tachometer in the coupling after removing the paddle shaft. The value of the constant $\frac{R^2}{4g}$ may then be calculated and the scale subdivided by means of the formula. This avoids the difficulty of measuring the radius of the tube with the required degree of accuracy.

9. PROPORTIONS OF OIL AND WATER

Fig. 5 shows the effect upon the rate of settling of changing the proportions of oil and water, using the two speeds of 900 and 1500 r. p. m. for each of the three oils. With more than 30 cc of oil the meniscus between emulsion and oil became indistinct and with less than 20 cc of oil the accuracy required in measuring out the oil would have been too great. As the figure showed that in general the minimum rate of settling was obtained with 20 cc of oil and 40 cc of water, these proportions were adopted as standard.

The question naturally arises in this connection whether the water may be taken from the faucet or whether it is necessary to use distilled water. Wells and Scott-Taggart¹⁹ say:

There is a peculiar delicacy in the chemical reactions that evidently take place, for tests of oil made with double-distilled water obtained from sources wide apart show no emulsion with one water and a strong emulsion with others.

Bryan used (1) distilled water at 65° F (18.3° C), (2) Severn River water (340 grains chlorine) at 65° F, and (3) boiling distilled

FIG. 5.—Effect of proportions of oil and water upon rate of settling

water, and found that with almost all oils the salt water gave a much greater amount of emulsion after standing. I have used Washington water as it comes from the faucet, distilled water, and water from an 80-foot well, but have never been able to

¹⁹ H. M. Wells and Wm. Scott-Taggart, *Power*, p. 188; Aug. 3, 1909.

detect any difference in results traceable to the difference in the water. While I can not confirm the statement of Wells and Scott-Taggart, it is evident that distilled water should be used, at least until experience showed that the city water available gave the same results.

10. REPRODUCIBILITY

Table 3 shows results of five successive tests with the same kind of oil, taking readings on the even minutes, to the nearest cubic centimeter.

TABLE 3
Check Determinations

Time since stopping paddle	Reading at upper meniscus, test No.—					Rate of settling per hour, test No.—				
	1	2	3	4	5	1	2	3	4	5
	cc	cc	cc	cc	cc	cc	cc	cc	cc	cc
4 minutes.....		53	53	53	54		105	105	105	90
5 minutes.....	51	50	49	51	51	108	120	132	108	108
6 minutes.....	48	47	46	48	49	120	130	140	120	110
7 minutes.....	45	45	44	45	46	129	129	137	129	120
8 minutes.....	43	44	42	43	43	128	120	135	128	128
9 minutes.....	42					120				120

Selecting the maximum rate of settling for each test, we have the demulsibility values of 129, 130, 140, 129, and 128 for the five tests, respectively.

While it is probable that more concordant results might have been obtained by taking readings at more frequent intervals, this will not ordinarily be necessary. In view of the great differences between commercial oils, and even between different samples of the same brand, a test which gives only fairly accurate results will usually serve to make a selection between a number of submitted samples.

III. FURTHER DETAILS OF PROCEDURE RECOMMENDED

1. TESTS FOR OILS OF VERY LOW OR VERY HIGH DEMULSIBILITY

It will be noted that in the tests shown in Figs. 2 to 5 the standard conditions of test (20 cc of oil and 40 cc of water, stirred for five minutes, at 55° C, at a speed of 1500 r. p. m.) have been used, except that the temperature was 5° C too low, and one condition was taken as a variable in each series. These standard conditions are suitable for oils with a certain range of demulsi-

bility, but they do not permit a distinction to be made between several oils all of which show a demulsibility of zero or of 1200. While no test for emulsifying oils has been settled upon, it may be pointed out here that the emulsifying effect may be reduced by decreasing the speed or by increasing the temperature or by using more than 20 cc of oil in the total of 60 cc of liquid.

On the other hand, if it were desired to increase the emulsifying effect so as to distinguish between oils of very high demulsibility the temperature could be decreased. An increase of speed or a decrease of the proportion of oil would not be of service.

2. SUPPLEMENTARY RULES AND PRECAUTIONS

In addition to the main features of the test which have been given above, the following rules are an aid to accuracy or convenience in making the test:

1. Care should be taken, by shaking the container in which the oil is received, and otherwise, that the oil which is used in the test is a fair sample.

2. If the oil is received in a glass bottle, care should be taken that it is not exposed to sunlight.²⁰

3. Care must be taken that cylinders and paddle are clean from one oil before testing another. After wiping the paddle with the finger, to avoid drainage losses, it should be wiped a second time with an absorbent body to avoid contamination of the fresh oil. If soap is used in cleaning the cylinders, especial care must be taken to eliminate all traces of soap in the final rinsing.

4. It is convenient, to save time, to adopt the rule that no oil shall be allowed to settle for a greater length of time than one hour, and take its demulsibility as the number of cubic centimeters of oil which have settled out in that time. While there are some oils which do not reach a maximum rate of settling in one hour, they are of such poor quality that, when engine oils are being considered, it is not necessary to distinguish between them. Oils which show no sign of settling at the end of one hour are said to have zero demulsibility.

5. It is convenient, and sufficiently accurate for most purposes, to take readings only on even minutes and to the nearest cubic centimeter.

6. If rule 5 is adopted, the highest possible demulsibility will be obtained if all the oil, 20 cc, settles out in one minute, or at the rate of 1200 cc per hour, and the demulsibility may be taken, without

²⁰ See U. S. Bureau of Standards Technologic Paper No. 73, p. 9.

calculation, from Table 4. If the scale of the cylinder were used which reads from the top down, the values in the first line of the table would run from 41 to 60, instead of from 59 to 40.

TABLE 4

Rate of Settling or Demulsibility of Oils (Expressed in Cubic Centimeters per Hour)

Elapsed time after stirring, minutes	Reading at upper surface of emulsion, cc																			
	59	58	57	56	55	54	53	52	51	50	49	48	47	46	45	44	43	42	41	40
1.....	60	120	180	240	300	360	420	480	540	600	660	720	780	840	900	960	1020	1080	1140	1200
2.....	30	60	90	120	150	180	210	240	270	300	330	360	390	420	450	480	510	540	570	600
3.....	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340	360	380	400
4.....	15	30	45	60	75	90	105	120	135	150	165	180	195	210	225	240	255	270	285	300
5.....	12	24	36	48	60	72	84	96	108	120	132	144	156	168	180	192	204	216	228	240
6.....	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180	190	200
7.....	9	17	26	34	43	51	60	69	77	86	94	103	112	120	129	137	146	155	163	172
8.....	8	15	23	30	38	45	53	60	68	75	83	90	98	105	112	120	128	135	143	150
9.....	7	13	20	27	33	40	47	53	60	67	73	80	87	93	100	107	113	120	127	134
10.....	6	12	18	24	30	36	42	48	54	60	66	72	78	84	90	96	102	108	114	120
11.....	6	11	16	22	27	33	38	44	49	55	60	65	71	76	82	87	93	98	104	109
12.....	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
13.....	5	9	14	19	23	28	32	37	42	46	51	55	60	65	69	74	79	83	88	92
14.....	4	9	13	17	21	25	30	34	39	43	47	51	56	60	64	69	73	77	81	86
15.....	4	8	12	16	20	24	28	32	36	40	44	48	52	56	60	64	68	72	76	80
16.....	4	8	11	15	19	23	26	30	34	37	41	45	49	53	56	60	64	68	71	75
17.....	4	7	11	14	18	21	25	28	32	35	39	42	46	49	53	56	60	64	67	71
18.....	3	7	10	13	17	20	23	27	30	33	37	40	43	47	50	53	57	60	63	67
19.....	3	6	10	12	16	19	22	25	28	32	35	38	41	44	47	51	54	57	60	63
20.....	3	6	9	12	15	18	21	24	27	30	33	36	39	42	45	48	51	54	57	60
21.....	3	6	9	11	14	17	20	23	26	29	31	34	37	40	43	46	49	51	54	57
22.....	3	5	8	11	14	16	19	22	25	27	30	33	35	38	41	44	46	49	52	55
23.....	3	5	8	10	13	16	18	21	24	26	29	31	34	37	39	42	44	47	50	52
24.....	3	5	8	10	13	15	18	20	23	25	28	30	33	35	38	40	43	45	48	50
25.....	2	5	7	10	12	14	17	19	22	24	26	29	31	34	36	38	41	43	46	48
26.....	2	5	7	9	12	14	16	18	21	23	25	28	30	32	35	37	39	42	44	46
27.....	2	4	7	9	11	13	16	18	20	22	24	27	29	31	33	36	38	40	42	44
28.....	2	4	6	9	11	13	15	17	19	21	24	26	28	30	32	34	36	39	41	43
29.....	2	4	6	8	10	12	15	17	19	21	23	25	27	29	31	33	35	37	39	41
30.....	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40
35.....	2	3	5	7	9	10	12	14	15	17	19	21	22	24	26	27	29	31	33	34
40.....	2	3	5	6	8	9	11	12	14	15	17	18	20	21	23	24	26	27	29	30
45.....	1	3	4	5	7	8	9	11	12	13	15	16	17	19	20	21	23	24	25	27
50.....	1	2	4	5	6	7	8	10	11	12	13	14	16	17	18	19	20	22	23	24
55.....	1	2	3	4	5	7	8	9	10	11	12	13	14	15	16	17	19	20	21	22
60.....	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20

EXPLANATORY NOTE.—The following examples illustrate the construction of this table: If the reading at upper surface of emulsion is 50 cc and the elapsed time is 15 minutes, the rate of settling or demulsibility $= (60-50) \times \frac{60}{15} = 40$ cc per hour; for a reading of 45 cc and a time of 10 minutes, demulsibility $= (60-45) \times \frac{60}{10} = 90$ cc per hour.

7. Much time can frequently be saved in case it is not necessary to get the exact value of demulsibility but only to find whether or

not the demulsibility is up to a specified value. This is an advantage in comparison with other methods of test which require that the emulsion must be set aside for an hour, 24 hours, or other stated length of time. For example, if a demulsibility of 300 is specified and the oil has not all settled out in four minutes it has failed to meet the requirements, and it is not necessary to wait until the maximum rate of settling is reached, or until the end of an hour, to find out, perhaps, whether the demulsibility is nearer to 25 or to 30.

8. The object in expressing resistance to emulsification by a single numerical value is to be able to describe the desired quality of the oil in a manner which could be enforced in a contract. I do not consider that the cloudiness of the separated water or oil or texture of the emulsion can be accurately enough described for this purpose except, perhaps, on the basis of tests requiring better laboratory facilities than available to most oil consumers. Such descriptions are of interest and should be reported, but in the great majority of cases the water separates out perfectly clear and the oil is nearly so. With the best nonemulsifying oils there is apparently no true emulsion, but only a kaleidoscopic movement of bubbles to be observed. With marine-engine oils the water not infrequently has a very milky appearance, which lasts for months.

When there is a large amount of water in the oil which settles out, as indicated by its volume being greater than that of the clear oil used to make the emulsion, this fact should, of course, be noted. I have not, however, considered it necessary to determine the exact percentage of water present, as in Conradson's²¹ test, because this information is of doubtful value to an engineer. It is not certain that an emulsion has necessarily less "lubricating value" than the original oil. As a general rule emulsions seem to have greater viscosity than the original oils, and this should slightly increase the friction, which, unless there is metallic contact, is proportional to the viscosity; but at the same time the bearing power will be increased, and metallic contact may be prevented, with a consequent decrease in friction. Heimann²² says:

Oils soluble in water, or emulsions of oil in water, have not yet been investigated, though from the criterion of the tests that have been made it would be expected that the lubricating value of such solutions or emulsions would be high, yet such investigations are at present being made.

Bryan²³ did some work on the same problem. Riemer²⁴ relates an experience with a bearing which was lubricated by a quite

²¹ P. H. Conradson, *Proceedings American Society for Testing Materials*, 16, Part II, p. 276; 1916.

²² H. Heimann, *Zeit. d. Vereines deutscher Ingenieure*, p. 1227; 1905.

²³ *Loc. cit.*, p. 561.

²⁴ J. Riemer, *Zeit. d. Vereines deutscher Ingenieure*, p. 654; 1895.

heavy mineral oil containing a small amount of water from the water-cooling system. He says that an emulsion was formed "which lubricated excellently (ausgezeichnet) and cooled at the same time."

3. OCCASIONAL DIFFICULTIES

When the test for demulsibility is applied to other oils than the high-speed engine and turbine oils for which it is primarily intended, difficulties may be encountered in obtaining readings. The following exceptions may take place to the normal motion of the menisci which has been described.

1. No emulsion at all may be formed, or the settling may take place so quickly that no emulsion is visible by the time the paddle has been withdrawn.

2. No meniscus may be visible at any time up to the end of an hour, in which case the demulsibility is zero.

3. If the oil is very dark, it may be difficult to distinguish any difference in color between the oil and its emulsion, so that the upper meniscus will not be visible. Unless it is possible to note a difference in texture between the oil and the emulsion, it is necessary to wait until practically all the water has settled out, and it is known that then the oil has practically all settled out, even if the liquid above the water is not at all clear and is in reality an emulsion containing 1 or 2 cc of water. The only objection to this procedure is that the maximum rate of settling, which has been named the demulsibility, usually occurs before all the oil has settled out, so that, while we wait, the moment when the maximum rate occurs may pass and the value obtained be, consequently, too low. However, it is to be expected, as a general rule, that oils with which this trouble will occur will be of so low a demulsibility that its exact value will not be a matter of great importance.

4. With some oils, under certain conditions, part of the water does not enter into the emulsion, and drops of oil are found adhering to the sides of the cylinder after the paddle is withdrawn. When this phenomenon occurs, the rate of settling, as indicated by the test when made in the usual way, is apt to be too high. In extreme cases the demulsibility might be called 1200 when the oil would emulsify readily under other conditions. The adhering drops are an important warning which should not be disregarded. This phenomenon is most apt to occur with very viscous or compounded oils, such as are used for gas or marine engines or steam-engine cylinders. The adhering drops may be avoided by using a lower speed or smaller proportion of water,

the total volume of oil and water being kept equal to 60 cc, as in Fig. 5. The rate of settling obtained under these changed conditions does not come under the definition of demulsibility.

If there is a suspicion that the adhering drops are present, it is simplest to lower the speed to, say, 1000 r. p. m. Then, if the maximum rate of settling obtained in other respects, just as when using the normal speed, is found to be less than when a speed of 1500 r. p. m. is employed, the adhering drops are surely present and the true demulsibility can not be obtained. Marine-engine oils have been found which would not emulsify at a speed of 1500 r. p. m., but gave a rate of settling of zero when the speed was reduced to 1000 r. p. m.

5. If part of the water does not enter into the emulsion, but the above-described phenomenon of adhering drops is not present, complete emulsification may sometimes be obtained by prolonging the stirring beyond five minutes or by increasing the speed.

IV. THEORY OF EMULSIFICATION

1. CAUSE OF EMULSIFICATION

Before proceeding with the account of the results obtained with the test for demulsibility the theory of emulsification will be briefly considered as it helps to explain them. Various theories are discussed by Bancroft, but for the purpose at hand it will be sufficient to point out that milk, a natural emulsion, is composed of globules of butter fat, coated with casein and suspended in water. In mayonnaise dressing the globules of oil are coated with the yolk of egg and suspended in vinegar. The object of the pharmacist, in making permanent emulsions, is first to thoroughly divide the oil into globules and then to surround each globule with an adhesive envelope to prevent them from reuniting. The lubricating engineer, on the contrary, desires that there shall be no substance present in the oil which might form an adhesive envelope in case the oil became finely divided. In other words, if nothing is present but a pure oil and pure water, any emulsion which may be formed has but little permanence.

As a general rule, a "pale" oil has been filtered more than a "red" oil, and the latter will emulsify the more readily. Job ²⁵ points out that it is the amount of filtering and not necessarily the lightness of color which distinguishes a good oil. He says:

Our investigations indicated that filtering to a light color, as, for instance, that of a "sun-bleached" oil, is unnecessary, since good results have been obtained with oil

²⁵ Robert Job, Proceedings American Society for Testing Materials, p. 614; 1909.

of fairly deep color even under exacting conditions; but the point of importance appeared to be that the oil had been filtered or else chemically treated in such a manner that the waxy substances, the so-called "amorphous waxes," had been completely removed. * * * It is known that the elimination of the waxes causes a decided increase in the ease with which the oil separates from hot water when thoroughly shaken with it, and this condition can be taken advantage of by prescribing that when 1 ounce of the oil is placed in a 4-ounce sample bottle with 2 ounces of boiling water, the bottle corked and shaken hard for one minute and let stand, the oil shall separate from the water within a specified time, depending on the nature of the oil, and that there shall be no appearance of waxy substances at the line of demarcation of the oil and water.

The above quotation referred to turbine oils. That the rule that pale oils emulsify the least also holds good for steam-cylinder oils is indicated by Wells,²⁶ who says:

It was found that, as a rule, dark cylinder oils much more readily emulsified than pale oils, that different waters had dissimilar effects on the same oil, enabling us to adapt an oil to special conditions or requirements as far as its emulsifying properties are concerned.

Proof that high demulsibility is an indication of thorough purification may be obtained by filtering an oil of low demulsibility through bone charcoal or fuller's earth. It was found possible to greatly improve the demulsibility of oils in this way.²⁷

2. THE TWO KINDS OF EMULSIONS

It is well known that there are two kinds of emulsions—the first consisting of drops of oil in water, as with milk; the second of drops of water in oil, as is the case with butter. Emulsions made by the pharmacist are of the first kind. The type of emulsion is not determined entirely by the relative amounts of oil and water, since there is a considerable range of proportions where either type may be obtained, depending on the method of agitation employed. Ostwald²⁸ made the assumption that the drops were all spherical and of equal size, so that the disperse phase (i. e., the liquid present in drops) changes into the dispersing phase as soon as the space for it has become so small that the drops touch each other. On this basis the limiting proportions would be 74.04 per cent of the disperse phase to 25.96 per cent of the dispersing phase.²⁹ Ostwald's assumption is, however, not entirely applicable, as he himself remarks, and Pickering obtained an emulsion with 85 per cent of oil in the disperse phase, using a syringe as a means of agitation. He says:

Although an emulsion prepared in the above-described manner can contain at most 85 per cent of oil, it is possible, however, to raise the oil content high above this value.

²⁶ H. M. Wells, *The Engineer*, p. 155; Aug. 14, 1903.

²⁷ C. E. Waters, *Technologic Paper of the U. S. Bureau of Standards*, No. 73, p. 9.

²⁸ Wa. Ostwald, *Zeit. Kolloidchemie*, 6, p. 103, 1910; 7, p. 64, 1910.

²⁹ See also E. C. Bingham, *Scientific Papers of the U. S. Bureau of Standards*, No. 278, p. 330.

If a strong emulsion is violently shaken with more and more oil, the oil content can be raised to 99 per cent. The remainder consists of a 1 per cent soap solution. The oil which was used was ordinary illuminating oil.

Ostwald, after describing his method of making tests, as already quoted, continues:

The first tests with the above methods showed that the use of new cylinders each time gave fairly comparable results. Yet repetition of the same test by reemulsifying the mixture after it had stood, also entirely new tests in cylinders washed with hot water, gave conflicting results. The supposition that the nature of the surface of the cylinder and paddle was to blame for the disagreement was strengthened by the observation that with new cylinders, according to which ingredient was poured in first, two extreme values resulted, and that the discordant results always lay in the region between these two extreme values. The difficulty was solved by careful cleaning of the cylinders and paddle or carefully preparing the entire surface which came in contact with the liquid to make conditions beyond suspicion in this regard. It was found, however, that the emulsion is very sensitive to the surface condition. A used and normally cleaned cylinder required treatment with chromic acid and hour long steaming until it is clean again, and gives results beyond suspicion.

The surfaces of cylinders and paddle, so cleaned and dried, were then prepared by either wetting with water (W) or by careful wetting with oil (O). This was done with the help of the measured amount of the ingredient in question intended for the test. Immediately before the test the second ingredient was added in the measured amount and the stirring began immediately. According as the surface was (W) or (O) the short-lived emulsions which were thus obtained had very different characteristics. The O emulsions were especially short lived and separated almost completely, in only a few minutes, into an upper oil layer (more exactly, a very permanent emulsion of a small amount of water as disperse phase and a large amount of oil as the dispersing phase) and practically completely clear water. With O surfaces the meniscus was always irregular (fetzig). The walls of the lower part of the cylinder also had adhering drops of oil.

The W emulsions—the usual emulsions—were incomparably more permanent. They separated slowly into a practically clear oil layer and an emulsion with water as the dispersing phase containing finely divided drops of oil. This emulsion was also very permanent as well as the long-lived water-in-oil emulsion formed with O surfaces. Meniscus and walls were always clean.

It is fortunate that it is not necessary to take all the precautions of Ostwald in order to get uniform results with our test. Possibly he was striving for a higher degree of accuracy than is needed in a technical test, or his difficulties may have been due to the nature of the oil or to his type of churn. The most significant point in his results is that when he had O surfaces, giving short-lived emulsions of drops of water in oil, he observed the phenomenon of adhering drops, while, on the other hand, with W surfaces more permanent emulsions of drops of oil in water were obtained and the cylinder surfaces were always clean. Ostwald gives as an illustration a mixture of 60 per cent of water and 40 per cent of kerosene, the O emulsion of which settled in about 6 minutes and the W emulsion in 30 minutes. This mixture can not be emulsified at all by the apparatus shown in Fig. 1.

In my tests, without taking any precautions to get O or W surfaces, as far as observed, the emulsions obtained consisted of drops of water in oil, as shown by the fact that the emulsions were thinned out by the addition of oil, but not by the addition of water. Microscopic examination confirmed this conclusion. I am unable to explain why Ostwald obtained clean cylinders with oil-in-water emulsions, while, as a general rule, I obtained clean cylinders with water-in-oil emulsions.

V. APPLICATIONS AND RESULTS OF PROPOSED TEST

1. RELATION BETWEEN DEMULSIBILITY AND OTHER PHYSICAL PROPERTIES OF OILS

Bryan³⁰ says "the specific gravity has no apparent effect on the lubricating quality of an oil, and also no apparent effect on the rapidity with which the oils settle out."

A more serious consideration is whether viscosity has any effect on demulsibility and whether the same degree of purity is indicated by a demulsibility of, say, 300 with one viscosity as if the same rate of settling were obtained with oil of another viscosity. According to Stokes's law,³¹ the final velocity which will be reached by a sphere falling through a viscous medium is given by the equation

$$V = \frac{2r^2gd}{9\mu},$$

where r is the radius of the sphere, d the difference in density of the sphere and the viscous medium, g the acceleration of gravity, and μ the viscosity of the medium. Thus, the more viscous the medium the slower would the drops settle out, and this is the general result of my tests. It should be noted in this connection that the viscosity of the emulsion may not be proportional to the viscosity of the original oils, and it is the emulsion which forms the medium in my tests.

I am inclined to believe that the slower settling of the viscous oils is caused by their being in general less pure, due mainly to the greater difficulty in purifying them. In speaking of cylinder oils, Schwarz says:

Clear mineral oil is, in general, more easily washed than dark oil containing asphalt, apparently because the asphaltic material easily holds back the soap and is, on its own account, difficult to separate from water. This may be the reason why a large majority of the cylinder oils tested here formed emulsions with water at 85° C.

³⁰ Loc. cit., p. 557.

³¹ Mathematical and Physical Papers, Cambridge University Press, 3, p. 55; 1880.

2. RELATION BETWEEN DEMULSIBILITY AND CHEMICAL TESTS

As pointed out, when speaking of transformer oils it is possible by means of stirring tests to detect smaller amounts of the emulsifying ingredient than is possible by chemical means, and this explains why it has been so often found by chemists that of two oils which appeared to be equally pure one would emulsify in use while the other would not. Table 5 slightly rearranged from Philip, gives experimental results which confirm the greater sensitivity of the stirring test. Philip says:

As far as the use of a mineral lubricating oil for turbines is concerned, the determination of the demulsification value is of greater use than any other test which can be made. * * * Out of between 700 or 800 samples of such oils which have been tested and passed as satisfactory as possessing demulsification values of 90 per cent or over, not a single one has given any trouble whatever due to the formation of emulsions under the practical conditions of use on a forced lubricating system on steam turbines.

He has unfortunately neglected to give the dimensions of his paddle and other details, so that it is not possible to duplicate his apparatus nor to find a conversion factor between demulsification value and demulsibility.

TABLE 5

Comparison of Demulsification Value and Chemical Tests, Rearranged from Philip's Values

Demulsification value of high-class special mineral turbine oils	Origin of fuel oil of which 1 per cent was mixed with oils in column 1	Per cent bitumen in added fuel oil—		Demulsification value of 1 per cent mixture	Per cent bitumen in mixtures as shown by amyl-alcohol method
		By amyl-alcohol method	By ether-alcohol method		
96	Shale oil, cracked.....	0.0	0.0	94	
94	Borneo.....	0.38	0.86	94	
94	Roumania.....	1.8	2.02	94	
94	Burmah, distilled.....	0.0	0.10	92	
94	Texas.....	1.0	1.44	92	
94	Persian.....	1.21		88	
92	Trinidad.....	7.1	7.78	74	
95	Persian.....	2.15	4.2	34	
91	Mexican.....	17.62	14.22	30	
98	Burmah, distilled.....	0.0	0.10	93	0.0
98	Borneo.....	0.38	0.86	90	0.0038
98	Texas.....	1.00	1.44	74	0.010
98	Persian.....	1.40	4.90	73	0.014
98	Roumania.....	1.80	2.02	64	0.018
98	Trinidad oil fuel.....	7.10	7.78	63	0.071
98	Trinidad Lake.....	11.75	11.64	57	0.1175
98	Mexican.....	26.25	20.50	27	0.2625

In Fig. 6 organic acidity and per cent carbonization have been plotted against demulsibility. Tests for acidity (expressed as the fraction of a milligram of KOH, potassium hydroxide, required to neutralize 1 gram of the oil) and for carbonization, as found by Waters's ³² method, were made by the division of chemistry of this Bureau as part of the routine testing of oils. The demulsibility tests were made with paddle No. 1, a temperature of 55° C, a speed of 1500 r. p. m. for five minutes, and the standard proportions of two parts of water to one part of oil. The figure shows that the great majority of points, for acidity tests, may be expected

FIG. 6.—Comparison of demulsibility with chemical tests

to lie below some such curve as A A. The point P is for a hydraulic-press oil, and its high demulsibility, relatively to its acidity, may be due to its very low viscosity.

It will be seen that there is a low demulsibility whenever there is a high acidity, but that a low value in the chemical test is not always accompanied by a high demulsibility. The per cent of ash bears a similar relation to demulsibility.³³ The relation between demulsibility and carbonization appears to be much less marked.

³² C. E. Waters, U. S. Bureau of Standards, Scientific Paper No. 160.

³³ W. H. Herschel, Proceedings American Society for Testing Materials, 16, Part II, p. 264; 1916.

3. STEAM-CYLINDER OILS

It is usually assumed that an emulsifying oil is desirable for use in steam-engine cylinders, except with superheated steam, on the ground that an emulsion will stick better to the wet cylinder walls than will the original oil. However, a few expressions of a contrary opinion may be found. Wells and Scott-Taggart say:

An emulsifiable oil renders the reuse of the water a difficult if not impossible matter, and in any case an expensive oil eliminating or purifying plant must be used to free the oil from water. Further, when the oil is in the form of an emulsion on the cylinder walls it is easily removed or washed away and therefore large quantities of oil are required to replace it, and it must be remembered that even then good lubrication is not being obtained because it is an emulsion that is lubricating the engine and not the pure oil, which may be an extremely good lubricant by itself.

Another opinion adverse to emulsifying cylinder oils is given by Holde,³⁴ who says:

Steam-cylinder oils should not contain any soaplike compounds, as these would cause the steam to form emulsions with the oil, which instead of lubricating would, under such conditions, be carried away with the condenser water (condensed steam). The following test is therefore useful: 10 cc of oil and 10 cc of water are shaken at 85° C (185° F) for one minute in a 20 mm (13/16 inch) wide test tube. An oil is considered as nonemulsifying if it separates after standing one hour at 85° C and if a layer less than 1 mm (1/32 inch) has formed between the oil and the water, and as weakly emulsifying if a 2 mm layer forms. If the oil does not separate from the water or if a layer thicker than 2 mm forms, it is emulsifying. Care must be taken in interpreting the result.

A possible reconciliation between the apparently conflicting opinions on steam-cylinder lubrication may be arrived at as follows: All oils become less viscous with an increase in temperature, and on this account hot surfaces are difficult to lubricate, since the carrying power is directly proportional to the viscosity.³⁵

With steam-engine cylinders the trouble may be partly due to the greater ease with which oils of low viscosity may be washed away from the cylinder walls.³⁶ Now the rate at which an oil will decrease in viscosity with an increase in temperature depends upon the viscosity and also upon the nature of the oil. Over the temperature range where lubricants are most commonly used, as a general rule, the fixed oils (i. e., the animal and vegetable oils) lose the least, paraffin-base oils come next, and asphalt-base oils lose the most in viscosity, although at high temperatures the relative position of the paraffin and asphalt base oils is reversed. If the oil contains soap, the loss of viscosity with a rise in tempera-

³⁴ D. Holde, *The Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes*, translated from the fourth German edition by E. Mueller, p. 159; 1915.

³⁵ M. D. Hersey, *Journal American Society of Mechanical Engineers*, p. 535, Sept., 1915; J. E. Denton; *Trans. American Society of Mechanical Engineers*, p. 369, 1887-88.

³⁶ G. H. Hurst, *Lubricating Oils, Fats, and Greases*, p. 316; 1911.

ture may be even more rapid. Now soap will cause an oil to emulsify, and it is generally true that the addition of a fixed oil will have the same effect, though to a lesser degree.⁸⁷ At first sight it would appear that the Holde test would discriminate against the cylinder oils containing the beneficial fixed oils or fats in the effort to eliminate the undesirable oils containing soap; but an examination of the results of Schwarz⁸⁸ with a test that is the same or similar to Holde's test shows that this is not the case. Schwarz gives his experience with a test for oils for locomotives, some of them using superheated steam, prescribed by the Eisenbahndirektion, Berlin, and in use since July, 1905. Oil refiners had raised the objection that there was no cylinder oil which would not emulsify with water at 85° C, and that this test ought not to be used as a measure of the value of an oil. Schwarz answers:

Evidently there is a misunderstanding. It is intended to show by the test whether soap-like substances are present. Mineral oils which are free from soap do not form an emulsion when shaken with water, the water separating in a short time from the oil, while oils containing soap form more or less strong emulsions according to the amount of soap present.

The results of Schwarz's tests, from 1905 to 1909, are given in Table 6.

TABLE 6

Schwarz's Emulsion Tests on Steam-Cylinder Oils

21 dark, pure, mineral cylinder oils:	
13 oils, including 4 for superheated steam.....	Strong emulsion.
5 oils, including 2 for superheated steam.....	Weak emulsion.
3 oils.....	No emulsion.
16 dark cylinder oils, containing fat:	
2 oils, including 1 for superheated steam.....	Strong emulsion.
11 oils, including 2 for superheated steam.....	Weak emulsion.
3 oils.....	No emulsion.

It will be noted that three of the oils containing fat did not emulsify, which indicates that the method of shaking (which is not described) is not violent enough to produce an emulsion with such oils, and that emulsions are produced only when soap or similar constituents with a strong emulsifying effect are present. The test, therefore, is justified, providing that any ingredient which will produce a strong emulsifying effect will also cause the oil to lose viscosity more rapidly with a rise in temperature. Emphasis is placed on loss of viscosity rather than on emulsi-

⁸⁷ Wm. M. Davis, *Friction and Lubrication*, p. 153; 1904.

⁸⁸ F. Schwarz, *Mitteilungen aus dem königlichen Material Prüfungsamt*, p. 22; 1909.

bility on account of the doubt as to whether an emulsion has less value as a lubricant than the original oil.

As far as steam-cylinder oils are concerned, therefore, it may be concluded that those showing strong emulsibility are undesirable, because usually they will contain soap and will decrease too much in viscosity between the temperature at which they are tested and the temperature prevailing inside the steam-engine cylinders.

4. TRANSFORMER OILS

Electrical engineers experience trouble with a thickening of transformer oils with use or formation of deposits in oils subjected to heat. This is known as "sludging." These deposits vary in appearance from pale-yellow soft masses to dark-brown or black hard masses, and are similar to the deposits which occur in steam-turbine oils after long-continued use. Transformer oils, as a rule, have a demulsibility of 1200, and since only very pure oils are suitable for this use an additional proof is given that high demulsibility is an indication of great purity. Digby and Mellis³⁹ say:

The presence of any soluble impurity in oil must tend to decrease its value as a medium offering a resistance to the flow of electric current. * * * The grading of oils according to specific resistance gives a fair indication of their purity. There is, however, a large range in the specific resistance depending on the presence or absence of impurities in an amount determinable qualitatively as "traces" rather than quantitatively as analytically ascertainable volumes. * * * As regards the reasonableness of expecting the oil refiners to work to a standard of specific resistance, we would point out that the standard of chemical purity exacted from copper refiners is specified by the specific resistance of the copper which must be obtained.

Michie⁴⁰ further emphasizes the necessity for pure transformer oils, and says:

Analysis of transformer deposits shows that these contain a considerable proportion of oxygen, and as the original oils are free from oxygen the only conclusion that can be drawn is that the formation of these deposits is brought about by the oxidizing influence of the air on the transformer oils. In all likelihood there is a simultaneous polymerization of the oxidized molecules. The quantity of sludge which separates out in the oxidation process is largely dependent on the degree of refinement of the oil.

Finally, Thomsen⁴¹ may be quoted to show that the problem of obtaining a suitable lubricating oil for high-speed machinery is not essentially different from that of obtaining good insulating oils:

In fact a properly refined turbine oil is quite suitable for a transformer oil. * * * In the lubrication of steam turbines the oil, mixed with a certain small amount of water,

³⁹ W. P. Digby and D. B. Mellis, *Journal Institute of Electrical Engineers*, 45, pp. 166, 209; 1910.

⁴⁰ A. C. Michie, *Journal Institute of Electrical Engineers*, 51, pp. 215, 218; 1913.

⁴¹ T. C. Thomsen, *Journal Institute of Electrical Engineers*, 53, p. 150; 1915.

air, and dirt circulates at a high temperature in the bearings and at a low temperature in the oil cooler. If the temperature exceeds 140° F (60° C) we have found that with some oils sludging takes place, due to the oxidizing influence of the impurities. As transformer oils are less liable to oxidize than turbine oils, the danger limit is undoubtedly higher than 140° F, probably in the neighborhood of 160° F (71.1° C).

It is interesting to note in this connection that there is a tendency among turbine designers to increase the bearing temperatures in order to decrease the friction, and that turbines have already been designed to run with a bearing temperature of 175° F (79.4° C).

These discussions in regard to transformer oils lead to the following conclusions:

1. Turbine or high speed engine oils need to be pure in order to remain serviceable for great lengths of time because subjected to oxidizing influences which cause an impure oil to quickly break down and deposit sediment.

2. The required degree of purity can not be determined by chemical tests. The more sensitive tests for specific resistance or dielectric strength would be suitable for transformer oils. These electrical tests might be equally suitable for steam-turbine oils, but the same result, the determination of purity, is more easily accomplished by means of an emulsifier.

5. DEMULSIBILITY OF COMMERCIAL OILS

Fig. 7 shows a frequency curve for 141 oils received by various Government departments and tested at the Bureau of Standards. Marine engine and other compounded oils are omitted. A classification of these oils, according to the purpose for which they were intended, is given in Table 7. The same 141 oils were used in preparing Fig. 6, but it was impossible, on account of crowding, to plot all the points. In view of the arbitrary nature of the definition of demulsibility, it seemed justifiable, for the sake of convenience, in Figs. 6 and 7 to depart from a strict adherence to a uniform scale.

TABLE 7

Classification of 141 Tested Oils

Kind of oil:	Per cent.
Automobile and gas engine.....	39.0
High-speed engine and turbine.....	16.3
Machine.....	11.4
Ammonia.....	10.6
Miscellaneous.....	22.7
Total.....	100.0

Each point in Fig. 7 indicates the per cent of the total number of oils falling within a certain class; that is, having a demulsibility

between the values selected as the limits of the different classes and given at the bottom of the figure. The figure shows that the majority of the oils on the market are either very bad or very good.

I shall not attempt to indicate what values would be proper to place in specifications or what demulsibilities would be required to

FIG. 7.—Distribution of oil samples according to demulsibility

give satisfaction in the use of different classes of oil. The General Supply Committee, which makes contracts for purchasing supplies for the executive departments and other Government establishments, has contracts in force in which a demulsibility of 300 is specified for turbine and spindle oils. This is approximately the value that would be obtained with a half and half mixture of kero-

sene and olive oil, with a volume of water equal to twice that of the kerosene and olive oil together. On the other hand, where an emulsifying oil is required, as in the case of a marine-engine oil or oil for the crank case of a Westinghouse engine, a demulsibility of zero should be expected.

6. DEMULSIBILITY OF USED OILS

Since oils become acid with use and emulsify more readily,⁴² it is to be expected that the demulsibility would decrease. In order to get some idea how rapidly this decrease takes place in ordinary power-house practice, a circular letter was sent to a number of large users of steam-turbine oils requesting samples of new and used oils. Table No. 8 shows the demulsibilities obtained from samples received, together with the comments of the users of the oils.

TABLE 8
Demulsibilities of Steam-Turbine Oils

Section I.—NEW OILS

No.	Demul-sibility	Comment
1.....	1200	Proved satisfactory.
2.....	192	Best satisfaction in use of any oil of this type.
3.....	1200 400	} These two oils are in use.
	71	
4.....	600	We have been asked to try this oil.
5.....	1200	Proves to be very satisfactory.
6.....	300	We have been using this brand for 10 years.
		Satisfactory for our use.

Section II.—USED OILS

No.	Demul-sibility	Months in use	Comment
7....	81	36	So far is very satisfactory.
8....	85	1	Have practically no difficulty.
9....	41	12	Results considered as satisfactory.
10....	3	24	Contemplating a change of oil.
11....	81	5	Has proven satisfactory.
12....	39	12	
12....	98	10	
12....	87	3	
13....	75	7	

⁴² Archbutt and Deeley, loc. cit., pp. 539, 554.

TABLE 8—Continued

Section III.—NEW AND USED OILS OF SAME BRAND

No.	Demulsibility		Months in use	Comment
	New	Used		
14....	150	74	2	
15....	280	93	12	This grade of oil has proved satisfactory.
16....	600	102	24	
17....	68	1	29	Oil still doing satisfactory services.
18....	168	0	120	25 per cent of fresh oil added since July, 1906.
19....	1200	12	11	Discoloration due to babbitt bearings.
20....	41	4	6	Deposit after six months' use.
21....	1200	114	60	
22....	94	32	10	
23....	80	23	20	
24....	120	102	2	Used this brand a great many years.

It will be noted that all the new oils of Section I of the table have a high demulsibility. With the exception of 71, for an oil not in use, the lowest value is 192. The lower demulsibilities of the used oils in Section II is very evident, the highest value being 98 after 10 months' use. The data of Section III, shown graphically in Fig. 8, give some idea of the rate at which the demulsibility might be expected to decrease, but for the following reasons very concordant results are not to be expected.

1. There is considerable inaccuracy in the assumption that deliveries of the same brand of oil are of uniform quality.

2. The conditions of use of the oils in the different power plants are very different, both with respect to speed and temperature of bearings and other causes tending to break down the oil, and also in regard to filters and settling tanks and means for keeping the oil pure and free of sediment.

3. It is usual practice to remove the oil periodically from the turbine in order to filter it more thoroughly than is possible by means of the small filter in the circulating system. Part of this oil will be thrown away and replaced by fresh oil, and the rest, if it appears to be good enough and "not too acid," will be returned to the turbine reservoir. Variations in this procedure and different degrees of thoroughness in cleaning out reservoirs and piping might cause the contamination of fresh oil before it was actually put in use at all, to be much greater at one plant than at another.

Fig. 8 shows that oils decrease in demulsibility with use, and that, as a general rule, oils of low demulsibility when new do not lose demulsibility as fast as those of higher demulsibility. It should be remembered in this connection, however, that the scale for demulsibility is a purely arbitrary one, and that it is not supposed that resistance to emulsification, if it could be expressed in cgs or some other rational units, would be exactly proportional

FIG. 8.—Demulsibility of used steam turbine oils

to demulsibility. I am unable to account for the apparent rapid deterioration of oil No. 19.

It seems probable that for any particular turbine in a given plant a value for the demulsibility could be found beyond which it would be unsafe to go, and that it would be an aid to the operating engineer to keep record of the demulsibility, as well as of the amount of sediment, in determining when the oil became unfit for use. The test for acidity might serve the same purpose, but it would require the services of a chemist, and, as shown by Fig. 6, it is less sensitive.

VII. SUMMARY

With forced-feed lubrication trouble is often experienced from an emulsification of the oil. Tests which have been proposed for the resistance of an oil to emulsification are either indefinite or are incompletely described, and therefore the following test has been devised:

One part of oil to two parts of water are stirred for five minutes in an ordinary 100 cc graduated cylinder at a specified speed and temperature by means of a flat, metal paddle. The emulsion thus formed is allowed to stand at the same temperature and readings taken at intervals of the volume of oil separated out. The maximum rate of settling, readily found without calculation from a table, is called the "demulsibility" and is used as a measure of the resistance of the oil to emulsification.

If oils of sufficiently high demulsibility are used, no trouble is experienced with emulsification. It has been found also that oils of high demulsibility will last longer in use before becoming unserviceable from the formation of deposits.

WASHINGTON, August 7, 1916.