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Official Notice.

ORDER OF MERIT.

His Majesty the King has been pleased to confer the distinction of the Order of Merit upon Sir Wm. Crookes, F.R.S., a member of the first Council of the Society.

Liverpool Section.

Meeting held at The University, on Wednesday, April 13th, 1910.

DR. JAMES T. CONROY IN THE CHAIR.

THE SEPARATION OF OIL FROM CONDENSER WATER BY ELECTROLYSIS.

BY RIDSDALE ELLIS.

This paper is the result of some experiments undertaken primarily to determine the reactions which take place in the Davis-Perrett electrolytic oil separator. These experiments led to an investigation of the properties of oil emulsions, more particularly in connection with the various methods in use for separating the oil from the water.

The Davis-Perrett oil separator was designed more particularly for separating the oil from condenser water, and has, as far as I know, been hitherto used only in that connection, but it may be used equally well for separating other emulsions or suspensions, as I will show later.

Before taking up the question of the separation of the oil from the condenser water, I will first review briefly the general properties of condenser water.

As is well known, the lubricating oil, when it reaches the hot cylinder walls, is so reduced in viscosity that it rapidly runs down to the lowest point of the cylinder and is either blown away through the exhaust or carried off by the drain pipe. The oil then is carried by the steam chiefly in the form of fine spray, and only to a certain extent as vapour. In the case of saturated steam the oil is carried as thin films of oil surrounding the drops of water. The usual method of separating the oil is, of course, to pass the steam through a baffle-plate separator, the water and oil being collected and run off together. The amount of oil carried away by the exhaust steam is only one part in five or ten thousand, and hence, however high may be the boiling point of the oil, a considerable part of the oil carried by the steam must necessarily be vaporised. This vaporisation is, moreover, greater on account of the fact that lubricating oils are a mixture of hydrocarbons of various boiling points, the lowest boiling constituents of which are readily vaporised at the temperature of the steam. It is evident therefore that separators placed in the steam pipe cannot remove all the oil, however well they may be designed. Some tests made at the Massachusetts Institute of Technology on baffle-plate oil separators show that the amount of oil separated out in this way is about 75 per cent. of the total oil contained in the steam. The remaining 25 per cent. of oil goes on to the condensers and is precipitated in the water in the form of very minute globules.

Where the lubrication of the engine is normal and an oil separator is placed in the steam pipe, the condensed water should not contain more than about one part in twenty-thousand of oil, the percentage being correspondingly higher if no separator is used. The drops of oil in this very dilute emulsion are extremely small, averaging only 0.00005 of an inch in diameter, and it is on account of their extremely small size that the difficulty of separating

them arises, and also gives to this emulsion the properties of suspensions and colloidal solutions. The size of the particles does not depend on the nature of the lubricating oil or on the method of their formation, for as Lewis* has shown, emulsions produced by distillation in steam contain globules of approximately the same size as those contained in other emulsions. The larger globules are, however, considerably larger than the average size found by Lewis, and probably these larger globules are those particles which were carried over mechanically by the steam, the smaller globules being those produced by condensation of the oil vapour.

A small amount of the oil contained in the water can be separated by flotation, but the velocity at which the globules rise through the water is extremely small even for those globules of average size, while, as Perrin† and others have shown in the case of gamboge and gum mastic emulsions, there is in any emulsion always a number of ultra-microscopic particles which will not separate out, however long the liquid containing them is allowed to stand.

In condenser water, after the larger globules have risen to the surface, a very stable, if very dilute, emulsion is obtained which may be kept for months without separating out completely. The chief characteristics of such an emulsion are dependent on the fact that the globules are electrically charged, which is shown by the fact that they migrate in an electric field. The striking feature to be noted with regard to the velocity of migration of these oil globules is that it is of the same order of magnitude as those of the majority of ions and of other suspensions and colloidal solutions. Not only does the close agreement between the velocity of migration of these oil globules and that of other colloidal solutions indicate that the emulsion may be treated exactly like a true colloidal solution, but the analogy is borne out by the fact that, as these oil globules are negatively charged, they can be precipitated by means of oppositely charged colloidal solutions, for example, colloidal ferric hydroxide.

Coagulation of the oil globules by means of electrolytes is impossible, owing to the extremely dilute nature of the emulsion. I might remark here that coagulation of an emulsion does not appear to involve in any way the coalescence of the oil globules, but is simply the aggregation of the minute oil globules into particles sufficiently large to be removed by filtration.

Returning now to the Davis-Perrett oil separator, this consists essentially in the electrolysis of the condenser water using iron electrodes, some electrolyte, usually sodium carbonate, being added to the water to raise its conductivity. Whatever the nature of the electrolyte, a basic salt is always produced on account of the alkali formed at the cathode. The precipitate formed entangles the oil globules, so that when the electrolysed solution is filtered all the oil is removed. Complete precipitation of the compounds of iron does not take place all at once, so that if the emulsion is filtered immediately the filtrate often contains colloidal ferrous compounds. If the emulsion is hot, as would be the case with condenser water, this colloidal solution is not formed.

If treated cold the electrolysed solution should be allowed to stand for a little time before filtering, the presence of precipitated iron compounds producing the precipitation of the remainder of the iron. I obtained an analogous result when the oil was precipitated by colloidal ferric hydroxide. In this case I found that above a certain concentration all the colloid was precipitated, however great the excess, that is, within limits. From this it appears that the presence of the coagulated colloid brings about in some way the precipitation of the excess of colloid added. The same is true in the case of electrolysis, the colloidal solution obtained being only precipitated in the presence of the coagula. With colloidal ferric

* Zeit. Chem. Ind. Koll., 1909, 211.
† Comptes Rendus 1908, 967.

hydroxide, the precipitation must occur on the surface of the oil globule, and the precipitation, which is apparently catalysed by the presence of coagulated ferric hydroxide, must continue as it began around the oil globule. The fact that the precipitation of the colloidal obtained by electrolysis only takes place in the presence of the coagula would point to the same mode of formation in the two cases. I then examined microscopically the precipitate produced, first, when the oil globules were coagulated by colloidal ferric hydroxide, secondly, when the precipitate was produced by the electrolysis of a sodium carbonate solution using iron electrodes, and thirdly, the precipitate obtained by precipitating basic ferrous sulphate in the water. The appearance of the precipitate produced in these three cases is exactly similar, which is a further proof that the electrolytic separation of the oil is extremely closely allied in its nature to colloidal coagulation, and consists in the precipitation of a positively charged compound around the negatively charged oil globules. Further, the similarity of the coagula shows that the function of electrolysis is merely to produce the precipitation in the water of a positively charged basic ferrous salt.

There have been various attempts made to separate the oil from the condenser water by precipitating substances therein, and the general idea of cleansing water from suspended impurities by means of flocculent precipitates is an extremely well-known mode of water purification. The principal substances used for the purification of water from suspended impurities are ferric and aluminium hydroxides and other voluminous precipitates.

I next made some experiments to determine whether the separation of the suspended matter depends on the electrical charges carried both by the suspended substance and by the precipitant, or whether it is merely a question of mechanical inclusion. Aluminium silicate is a good example of a flocculent precipitate, but when this substance is precipitated in an emulsion the oil is not coagulated in any way, as can be seen from the photograph, which illustrates the mechanical inclusion of the oil globules by means of aluminium silicate. The precipitate being white does not show up in the micro-photograph.

I then noticed that Pickering* stated that colloidal ferric hydroxide and basic salts were good emulsifiers, but that aluminium silicate would not emulsify oil at all. From these and other experiments now being made, it would appear that the electrical charges carried by the oil and by the emulsifier play an important part in the phenomena of emulsification.

While the cause of this precipitation on the surface of the oil globules is probably the difference in the electrical charges carried by the oil globule and by the precipitating substance, the surface tension at the oil-water interface will also have considerable influence. These two effects are most likely very largely inter-connected, but it should be remarked that, according to Cohen's† law, all substances suspended in water are negatively charged with the exception of hydroxides and basic salts. Hence the basic ferrous carbonate formed by electrolysis, and the basic ferrous sulphate formed by chemical precipitation are both positively charged, and so should precipitate on the surface of the oil globules, as has been shown to be the case.

Further, it is well known that agitating water with various substances, followed by sedimentation or filtration, will remove bacteria and other suspended solid matter. This principle has been applied to the separation of oil from condenser water by Dehne, who uses alumina for this purpose. He adds hydrated alumina made into a cream with water to the emulsion and filters the mixture. The oil is thereby retained by the alumina. Here again the electrical charges on the oil or on the bacteria or other suspended matter appear to play an essential part. If finely-powdered animal charcoal, which is positively charged, is shaken up in an emulsion and the liquid allowed to stand, the particles of charcoal carry down with them globules of oil. This is practically a case of the precipi-

tation of two oppositely charged suspensions, and is therefore analogous to the precipitation of one colloidal solution by another.

If, then, oil globules will collect small particles of certain solids around them, the filtering of an oil emulsion through a large mass of these substances should filter off the oil and give a clear filtrate. This is exactly what was found to be the case. Filtering media formed of the following substances give a clear filtrate:—Hydroxides of iron, aluminium, chromium, and calcium, barium carbonate, bone black, spongy iron and fine ground coke; but when barium sulphate, lead chloride and cotton-wool were used little or no oil was removed.

The filtration of emulsions has been recently dealt with by Emil Hatschek*. He found that filtration through magnesium or calcium carbonate would remove all the oil. Now Perrin has† shown that barium carbonate is positively charged, and in view of the preceding experiments it appears very probable that the separation of the oil by filtration through calcium carbonate or causticising mud is due to the difference in sign of the electrical charges carried by the oil and the filtering medium.

In an experiment of Spring‡ with regard to the filtration of a suspension of lamp black, the particles of carbon being positively charged, and the cellulose of the filter being negatively charged, all the black was retained. A little soap solution was added to the solution when the sign of the charge on the lamp black particles was changed, and when the liquid was filtered none of the carbon was retained by the filter.

Evidently then, the essential function of an electrolytic oil separator is to provide a simple and automatic means for precipitating in the water a basic ferrous salt, and in place of it we may use various filtering media or precipitate various flocculent precipitates in the solution.

These remarks apply almost equally well to the separation of all suspensions, since practically all suspended particles are negatively charged and will, therefore, behave in an exactly similar way to the oil globules. For instance, I have electrolysed with iron electrodes the effluent obtained from the Bradford wool suds after the wool-grease and other fats have been removed; the result is a clear filtrate free from all suspended matter, and apparently other effluents can be treated in a similar way. I then made some determinations in order to find out exactly how much of the oil is removed by this process. Since the oil in the emulsion rises gradually to the top of the liquid and adheres so strongly to the other oil particles on the surface, that these visible agglomerates cannot be completely broken up by shaking, some other substance must be used as a standard of turbidity. For this purpose soap solutions of various concentrations were used.

To compare the turbidity of two given liquids, such as an oil emulsion and soap solution, by means of transmitted light is very difficult, since evidently the precision of this method decreases as the percentage of the light cut off decreases. In other words, for small concentrations of oil the determination of the amount of turbidity to any degree of accuracy becomes impossible. To overcome this trouble, and to get a quicker way of determining the content of oil, a simplified form of Richard's "Nephelometer" was employed. This apparatus was designed by Richards§ for the comparison and estimation of opalescent precipitates, and depends not on the amount of transmitted light cut off, but on the amount of light reflected by the solid particles in the liquid. The light reflected is proportional to the amount of suspended material. In the simplified form used for these experiments, two test-tubes are taken, the rims being cut off so that black paper tubes can be readily slid up and down the tubes. The ends of these tubes are covered with black paper to cut off any reflection in the curved ends. On looking down the black tubes into the liquid only the light reflected by

* J. Chem. Soc., 1907, 81, 2001.

† Ann. Phys., 1892, 64, 217.

* This J., 1910, 29, 125.

† J. de Chim. Phys., 1904, 2, 801.

‡ Rec. Trav. Chim. Pay-Bas., 1909, 28, 120.

§ Ann. Chem. J., 1904, 31, 235.

the particles in the liquid is seen. The relative turbidity is then obtained by sliding up and down the black tubes until the amount of light reflected or the apparent turbidity is the same in both tubes. Then the amount of oil in each tube is of course inversely proportional to the length of tube exposed to the light.

Using this apparatus, the efficiency of separation in the Davis-Perrett apparatus was found to be over 98.5 per cent., the actual amount of oil still contained in the water after treatment being less than one part in a million. This amount of oil is so small that it is impossible to detect it by the direct comparison with distilled water, and the turbidity can only be detected by means of a Nephelometer. I cannot give accurate figures for the separation of oil by means of filtering materials, though in the case of coke it would appear to be over 95 per cent., and a similar or higher efficiency for filtration through red ochre.

After the efficiency of the Davis-Perrett apparatus as a separator, the next question is the cost of operation. The two principal items are the electrical energy consumed and the soda or other substance added to the water.

Using an emulsion of pure oil and pure water containing 1 part of oil and 20,000 of water, which is about the maximum content of oil ordinarily obtained in condenser water, I found that the minimum amount of electricity required was about 135 coulombs per gallon of water treated. This result was obtained on a small laboratory apparatus, but is I think sufficient to show the order of magnitude of the electrical energy required and to base one or two calculations as regards cost of operation.

The following calculations were based on the assumption that bipolar electrodes are used, and that the current efficiency is 100 per cent. Where iron electrodes are used in a very dilute sodium carbonate solution the decomposition voltage is about 1.50 volts, but I found that efficient bipolar action can be readily obtained by making the holes in the plate or the spaces round the plate small. Using 50 iron plates, the current required for treating 1000 gallons of feed water per hour will be 1.75 ampères, and at 230 volts, the watts per hour will be 227—a ridiculously small amount. With electricity at 2d. a unit the cost of the current works out at a halfpenny per 1000 gallons of feed water treated. The next item is the sodium carbonate added to raise the conductivity to the necessary amount. To each 1000 galls. of feed water 1.5 lb. of sodium carbonate must be added. With carbonate at £5 10s. per ton the cost per 1000 galls. is then a fraction less than 1d. The last item is the renewal of the iron plates. As these plates are used as bipolar electrodes, they should be not used after their thickness is much less than $\frac{1}{4}$ -in. However, reckoning on a twelve-hour day, the iron plates should be renewed every two years, so the cost of renewal need not be considered. These figures are based on the minimum amount of electricity and sodium carbonate, but it is evident that the cost is so slight that these amounts may be very considerably exceeded without making the cost prohibitive.

Except for the addition of the sodium carbonate solution the apparatus requires no attention, for a self-flushing filter which will cleanse itself periodically is usually installed.

The apparatus may be further simplified by adding tap-water instead of sodium carbonate solution, the calcium and other salts acting as the electrolytes. The amount of salts introduced will be less than that contained in ordinary hard water. Thus supposing the water added contained only calcium carbonate, sufficient would have to be added for the condenser water to contain 9.0 grains per gallon. Chloride solutions may be added in place of carbonate and hence sea-water may be used if desired.

There is a further consideration, and that is, what will be the effect on the boilers of a solution of a carbonate or other salt which has been electrolysed. Since alkali is always formed at the cathode and the precipitate formed is not pure hydroxide but a basic salt, there will always be a slight excess of alkali in the water introduced into the boilers. Since the water is very faintly alkaline, and since

the corrosion of iron is proportional to the content of hydrogen in the water, the amount of corrosion will probably be less than is the case in ordinary pure water.

Further, the apparatus appears to have a considerable field for use, not only in connection with the separation of oil from condenser water, for which it was primarily designed, but also for the treatment of other suspensions and colloidal solutions, and its cost in many cases would not appear to be prohibitive.

I take this opportunity of expressing my thanks to Prof. Goodwin, of the Massachusetts Institute of Technology in Boston, and also to Prof. Donnan, of this University, for their help and the many suggestions which they have made during the course of these experiments.

DISCUSSION.

Professor F. G. DONNAN thought that the great thing that Mr. Ellis had pointed out in this work was that the action of the Davis-Perrett electrolytic apparatus was simply the production of a basic ferrous precipitate to coagulate the oil. He presumed that a certain quantity of soda was added to the water to make it conduct. The positively charged basic precipitates were electrically adsorbed by the oil particles, and they enable the oil particles to aggregate together in groups. That seemed to him the essential point. Mr. Ellis had brought out the fact that the inventors of the process knew very little about electricity, as he had shewn that a ridiculously small number of watts are really required. The second point Mr. Ellis had made clear was that filtration was largely dependent on the electrical charges on the filtering medium and the matter filtered.

Dr. J. E. SOUVRICOMBE said that the apparatus had given considerable trouble in the cases he knew of. In working with cylinder oils he had found that metallic soaps were produced by the oxidation of hydrocarbon oils and their subsequent action on the finely-divided particles of metal abraded from the cylinder walls. Perhaps the presence of these metallic soaps might affect the stability of the emulsion.

Mr. HADFIELD remarked that a great amount of oil was lost by being mixed with water, and a great deal lost by emulsification. It was only mechanically mixed, and his experience was that a little water combined with some impurities carried through with the steam, caused the oil to be so mixed with the water that it could not be separated by ordinary means, and if this apparatus could be applied it would be a very good thing.

Mr. RIDSDALE ELLIS said that he had found that when he electrolysed emulsions cold he was liable to get colloidal iron substances in the filtrate. The sample he had shewn, he had had to warm before passing it through the electrolysing tank, otherwise there would be a considerable amount of colloidal iron found there. That was the principle difficulty he had found with the process. The question of the oxidation of hydrocarbon oils and the formation of metallic soaps had been brought up. He had tried evaporating some of the water obtained from the condenser, and he had found that when evaporated to a small volume a number of films were formed which separated out, and he had often wondered what was the nature of those films. Probably they consisted of metallic soaps. The question had also been brought up as to how crank chamber emulsion could be treated in order to obtain the oil from it. Experiments were made with regard to the separation of oil from a mixture of oil and water. It was found necessary to treat it with hydrochloric acid, to break down the layer of emulsifier at the surface of the globules and enable them to coalesce. The broken oil or any other oil which was emulsified could be de-emulsified by treatment with some re-agent which would dissolve the film. In some cases, as in the case of oil obtained from the steam separator, hydrochloric acid might be used. The re-agent used depended on the nature of the emulsion. The separation, or de-emulsification, was probably to some extent due to a change in the electrical charge carried by the oil particles.