point which seems to stand seriously in the way of a definite assertion that its existence has never been established is the specific statement by Frommherz, who had worked extensively among manganese compounds, as to its having been described by Scheele, while a demonstration to the contrary is not forthcoming. Perhaps some chemist may be able to say where, if at all, Scheele deals with the matter.

With regard to the compounds described by Descamps[1] and by Baudran[2] as containing potassium and manganese in combination with the tartaric acid radical, these may be assumed to contain the latter metal in the manganic state. There are difficulties in reconciling the formulas given by both authors with the analytical data which they advance, but a review of manganic compounds lies beyond the scope of this communication.

In conclusion, the author wishes to acknowledge, with thanks, his indebtedness to Miss Porter and to Mr. Barker for their valuable aid in dealing with the crystallographical matters included in this paper.

EDINBURGH, SCOTLAND.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF NATIONAL CARBON CO., INC.]

EMULSIFICATION OF WATER AND OF AMMONIUM CHLORIDE SOLUTIONS BY MEANS OF LAMP BLACK.

BY WILLIAM C. MOORE.

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Introduction.

Following the recent publication of results by Schlaepfer[3] on the emulsifying action of lamp black on water-kerosene mixtures, a considerable amount of time has recently been devoted in this laboratory to a study of the emulsifying action of various kinds of carbon on water and on aqueous solutions. At the outset it can be stated that the only successful emulsions with kerosene as the external phase, have been prepared by the use of lamp black as the emulsifying agent. Highly calcined lamp black and calcined petroleum coke were entirely unsuited for this work, probably owing to their inability to form a coherent film in the "dineric interface."[4]

In our work we have used successfully, as emulsifying agents for water and certain ammonium chloride solutions, several samples of commercial lamp black which had been prepared by the incomplete combustion of creosote oils. Since our results seem to bring out clearly certain surface phenomena underlying emulsion formation, it may be of interest to make them public, in the following report:

[1] *Compt. rend.*, **70**, 813 (1870).

[2] *Ann. chim. phys.*, [7] **19**, 555 (1900).

[3] *J. Chem. Soc.*, **113**, 522 (1918).

[4] Bancroft, *J. Phys. Chem.*, **19**, 275 (1915).

Experimental.

The procedure followed was very simple. A definite quantity of lamp black was weighed out and a definite volume of kerosene run in; a definite volume of water or of an aqueous solution of ammonium chloride was then added and the mixture stirred by an electrically operated stirrer for a definite time. A small portion of the emulsion was then examined under a micrometer microscope, care being taken to get on each slide a representative sample of emulsion. As a rule, 10 droplets, representative as far as possible of the slide, were measured for each preparation.

The major part of the work was with an ordinary commercial kerosene having a density of 0.8149 at 15°.

All the emulsions formed were with water or the aqueous solution as the disperse phase, and the oil the continuous phase. This was easily shown by the fact that water would not mix with the emulsions while kerosene would.

The conditions for each set of experiments are given in the following tables:

TABLE I.[1]

The Effect of Changing Amount of Lamp Black on Size of Particles.

A. Raw Black Sample No. 1, 15 cc. (old) kerosene and 25 cc. water.

Amt. black. G.	Time mixed. Min.	Diam. of particles. Mm.	Av. dev. %.	Remarks.
0.10	24	0.1201	69.9	Very poor emulsion: Most black settled out
0.40	30	0.1240	42.8	Fair emul.
0.40	30	0.1423	33.6	Fair emul.
0.60	30	0.1195	41.7	Fair emul.
0.80	30	0.0955	38.0	Fair emul.

B. Raw Black No. 1. Extracted with benzene until free from oil.

Kerosene: Water: Time of mixing 30 min.

Wt. Black. G.	20 oil : 20 H_2O.		15 oil : 25 H_2O.	
	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.
0.4	0.0895	20.5	0.1090	41.9
0.6	0.0706	26.5	0.0634	34.4
0.8	....	..	0.0907	23.9

C. Raw Black No. 1. Kerosene: *N* ammonium chloride. Mixed 30 min.

Wt. black. G.	30 cc. oil : 10 NH_4Cl.		25 oil : 15 NH_4Cl.		20 oil : 20 NH_4Cl.		15 oil : 25 NH_4Cl.	
	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.
0.2	0.0936	37.0	0.0735	36.2	0.0908	38.8	0.0558	22.7
0.4	0.0760	16.5	0.0916	47.7	0.0822	20.3	0.0607	26.10
0.6	0.0452	19.7	0.0721	35.5	0.0829	31.5	0.0533	30.0
0.8	0.0521	43.0	..	..	0.0628	24.6	...	..
..	..	..	..	..	...	..	...	..

[1] The results in Section E are by Miss Mary Mitchell.

TABLE I (*continued*).

Wt. black. G	10 oil : 30 NH_4Cl. Diam. Mm.	Av dev. %
0.4	0.0590	33.0
0.6	0.0400	31.02
0.8	0.0338	25.7

D. Raw Black No. 1; 15 cc. kerosene; *N* ammonium chloride, varied as shown; 30 min. mixing.

Vo. NH_4Cl. Cc.	5.		10.		15.		20.		25.	
Wt. black. G.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.
0.10	..	..	0.0703	19.1	0.1037	17.3	0.1095	17.8	0.1086	27.8
0.2	0.0760	16.5	0.0400	17.2	0.0406	17.2	0.1035	40.3	0.0558	22.7
0.3	0.0452	19.7	0.0513	17.6	0.0822	20.3	0.1002	15.8	0.0983	17.1
0.4	0.0521	43.0	0.0696	15.3	0.0615	38.4	0.0582	26.3	0.0607	26.1
0.5	0.0519	35.9	0.0492	25.5	0.0579	49.0	0.0659	55.8	0.0693	42.6
0.6	0.0566	42.1	0.0358	36.0	0.0628	24.6	0.0457	42.4	0.0533	30.0
0.75	0.0541	27.8	0.0376	34.6	0.0502	27.2	0.0529	51.1	0.0729	29.0

E. Raw Black No. 1; kerosene; 5 *N* ammonium chloride; 15 cc. kerosene, 0.5 g. black; ammonium chloride varied as shown. See (B) for significance of figures. Three separate runs made, under similar conditions. Five measurements each run.

	5.		10.		15.		20.	
NH_4Cl. Cc.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.
Run No. 1.....	0.0478	12.1	0.0440	31.8	0.0694	34.8	0.0930	49.6
Run No. 2.....	0.0482	8.7	0.0500	11.2	0.0629	52.6	0.1050	24.8
Run No. 3.....	0.0470	17.0	0.0536	22.0	0.0628	14.3	0.1044	9.6
Average.....	0.0477		0.0492	..	0.0650	..	0.1008	..

In Tables I, A, B and C above, the total volume of the liquid was kept at 40 cc. Reading downward, in the columns in these tables, showing the size of particles, the general tendency is seen that with the larger amounts of lamp black smaller particles are formed. In Tables I, D and E above, the amount of kerosene was kept at 15 cc. and the ammonium chloride varied. Reading from left to right, the general tendency is seen for the size of droplets to increase as the total volume of liquid increases. For constant volume of liquid, an increase in the amount of lamp black results in a general decrease in size of droplets, as can be seen from the vertical columns in D, showing droplet diameters.

From Tables I, A, B, C, D and E, the general conclusions can thus be drawn that an increase in the amount of lamp black in a given mixture of oil and aqueous solution or water causes a decrease in size of emulsified droplets of water.

This is to be expected, since for a given lamp black, a large weight of material has a greater surface than a small weight, so the given volume of disperse liquid must increase its own surface, *i. e.*, break into small droplets in order to take care of the larger surface by wetting.

As corollary to this proposition, it may be stated that in mixing two immiscible liquids with an emulsifying agent, the greater the amount of emulsifier the more thorough mixing.

TABLE II.

The difference between the emulsifying effects of raw lamp black and lamp black extracted with benzene.

A. Emulsions of water, kerosene and lamp black. Original lamp black No. 1 and same black extracted with benzene until all oils were removed, and dried.

Total volume of liquid, 40 cc. Figures at head of columns indicate cc. of water in 40 cc. of volume, the other portion of the liquid being kerosene. Time of mixing, 30 min.

		25.			25.			25.	
Material.	Wt. G.	Diam. Mm.	Av. dev. %.	Wt. G.	Diam. Mm.	Av. dev. %.	Wt. G.	Diam. Mm.	Av. dev. %.
Raw.....	0.40	0.1240	43.8	0.60	0.1195	41.7	0.80	0.0955	38.0
	..	0.1423	33.6	..	..	..	..	..	..
Extracted..	0.40	0.1090	41.9	0.60	0.0634	34.4	0.80	0.0907	23.8

B. Emulsion of *N* ammonium chloride, kerosene, lamp black. Same lamp blacks used as in II A. Total volume, 40 cc.; 0.40 g. of lamp black used in all cases. Time of mixing, 30 min.

Cc. *N* NH_4Cl.	10.		15.		20.		25.		30.	
	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.
Raw.....	0.0760	16.5	0.0916	47.7	0.0822	20.3	0.0607	26.1	0.0590	33.0
Extracted.....	0.0745	48.6	0.1202	35.9	0.1131	58.1	0.1104	50.9	0.1267	68.3

In A, the smaller particles obtained by use of purified lamp black, shows that the oils in the raw lamp black do not allow water readily to wet raw lamp black. On the other hand, *N* ammonium chloride wets raw black more readily than purified black. The reason for this is not known. Possibly the relatively slight elevation of temperature suffered by the lamp black in treatment with benzene in the extraction apparatus tends to agglomerate the finer particles into larger groups. The experiments with water would shed no light on this point, since the oils in raw lamp black are not readily wet by water.

Purified lamp black is thus seen to be a better emulsifier for water in oil; raw black is better for ammonium chloride solution.

In A it is shown that *N* ammonium chloride solution, under the same conditions, gives smaller droplets than does water and therefore that it wets raw lamp black more readily than does water. In B, water, giving smaller droplets than does ammonium chloride solution, is seen to wet purified or extracted lamp black more readily than does ammonium chloride. This result could be predicted from the higher surface tension of *N* ammonium chloride solution.[1]

[1] At 10° for 9.11% solution, 76.32 dynes per cm. as against 74.0 dynes per cm. for water at the same temperature; *Landolt and Börnstein*, 4th Ed., p. 112.

TABLE III.

The relative wetting action of water and of N ammonium chloride solution on raw and extracted blacks.

A. Raw Black; 15 cc. of kerosene; 25 cc. of water or of ammonium chloride solution.

	Wt. black. G.	Diam. Mm.	Av. dev. %.	Wt. black. G.	Diam. Mm.	Av. dev. %.
Water	0.40	0.1240	43.8	0.60	0.1195	41.7
	..	0.1423	33.6	..	..	..
NH_4Cl	0.40	0.0607	26.1	0.60	0.0533	30.0

B. Extracted black. Figures at head of columns give amount of water or of ammonium chloride in 40 cc., the remainder being kerosene. 0.40 g. of black used.

	15.		20.		25.		30.	
	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.	Diam. Mm.	Av. dev. %.
Water	0.0797	40.0	0.0895	20.5	0.1090	41.9	0.1208	47.5
NH_4Cl	0.1202	35.9	0.1131	58.1	0.1104	50.9	0.1267	68.3

TABLE IV.—EFFECT OF TIME OF MIXING.

All the work given above was for a constant time of mixing 30 min. For a constant ration of kerosene to N ammonium chloride solution of 10 cc. of the former to 30 of the latter raw black yielded the following results for varying the time of mixing:

Wt. black. G.	Time, 15 min. Diam. Mm.	Av. dev. %.	30 min. Diam. Mm.	Av. dev. %.	45 min. Diam. Mm.	Av. dev. %.	60 min. Diam. Mm.	Av. dev. %.	75 min. Diam. Mm.	Av. dex. %.	90 min. Diam. Mm.	Av dev. %.
0.40	0.0551	35.2	0.0590	33.0	0.0484	24.8	0.0504	38.7	0.0637	58.8	0.0949	41.0
0.60	0.0452	20.3	0.0400	31.2	0.0432	46.3	..	..	0.0490	17.0	0.0697	42.8
0.80	0.0367	30.6	0.0338	25.7	0.0250	20.9	0.0337	41.2	0.0265	49.6	0.0309	46.3

Apparently the size of droplets for any given mixture passes through a minimum when the time of stirring is varied. The variation in size of particles is still great, however, as shown by the high average deviation from the mean values. It would be impossible to tell when this minimum is reached except by actually carrying out the experiment. Accordingly an arbitrary choice of mixing time seems the only feasible method of mixing when a large number of experiments is being run, as in the present work. Table IV, however, brings out very clearly the point made in discussing Table I, that increasing the amount of lamp black gives smaller droplets in a given mixture.

TABLE V.

Results obtained with different raw blacks under the same conditions; total volume, 40 cc. 25 of water and 15 of kerosene; time mixed, 30 min.; 0.40 g. black used. (Original No. 1 was the black used in all above work).

	Run No. 1.		Run No. 2.	
Sample.	Diam. Mm.[1]	Av. dev. %.	Diam. Mm.	Av. dev. %.
Original black No. 1	0.1240	43.8	0.1423	33.6
Dated 12/10/18	0.1017	42.3	0.1041	28.8
Dated 12/14/18	0.1171	51.9	0.1062	41.7
Dated 12/16/18	0.1125	33.4	0.1399	41.3

[1] Mixed 32 minutes.

At first sight the results given would seem to indicate that it might be possible to differentiate between various lamp blacks by the size of particles afforded when the lamp black emulsifies water in kerosene. However, the *average deviation* from the mean is so great that the results from one lamp black overlap all the others; this method, therefore, is valueless as a means of distinguishing types of black.

General Discussion.

In every slide examined, whether water or ammonium chloride solution was used as the disperse medium, particles of a large number of sizes were to be seen. This is indicated by the uniformly high average deviation from the mean diameter. However, a qualitative inspection of any particular slide showed whether large particles (0.20 mm. or over), medium particles (0.10 mm.) or small particles (under 0.10 mm.) predominated, and attempts were made to measure, in general, particles of the predominant size on each slide. The great average deviation in size precludes any rigid mathematical treatment involving the extent of surface presented by the lamp black in the various emulsions.

In those cases where little water and little lamp black was present, there was always considerable free black in the oil even though emulsification was poor. Some of the emulsions, notably those in which 0.5 g. or over of lamp black were used in 30 cc. (Table I, D) were firm and stiff, of a buttery consistency and were stable even after standing several days.

When the emulsion as a whole was not stable a separation into two phases would generally occur. The upper consisted of kerosene, the lower of water emulsified in the remainder of the oil.

There was thus a tendency for the various emulsions with a definite black content to assume the same composition of oil and water, and thus to give the same size particles. This is seen in Table I, C, where the horizontal rows of figures for 0.2, 0.4 and 0.6 g. of lamp black do not show any regular tendency for the droplet size to change as the proportion of kerosene to ammonium chloride changes, the total *volume* of liquid remaining constant.

If we turn to Table I, and compare the results for 0.5 g. of lamp black in D, using N ammonium chloride solution, with those of 0.5 g. in E, using 5 N ammonium chloride solution, it is seen that the more concentrated solution gives the larger droplets. Here again the effect of the greater surface tension of the more concentrated solution is seen. The commonly accepted views on the influence of surface tension in determining the emulsoid condition of a mixture are thus strikingly confirmed.

The results with mixtures of lamp black and kerosene with ammonium chloride solution or water are striking in contrast to the behavior of lamp

black with water, kerosene or ammonium chloride solutions alone. Thus, raw lamp black when shaken with water or N ammonium chloride solution simply rises to the surface of the liquid, the oil content probably preventing much wetting.

Shaken with water, purified lamp black forms a suspension; with N ammonium chloride solution the lamp black again quickly rises to the surface. With kerosene, both raw and purified lamp blacks sink to the bottom of the containing vessel. The coloration imparted to the kerosene by the raw lamp black indicates the extraction of some of the oils by the kerosene.

Finally it should be noted that the water globules investigated in this research were in general larger than those reported by Schlaepfer,[1] thus indicating that our black had less "covering power" than the "gas black" used by him.

Summary.

The experimental results indicate that, while there are differences between different lamp black samples in their emulsifying power, the experimental error is so great that we cannot use this means for making definite positive tests as to the quality of a black.

From a different viewpoint the results with lamp black are of interest, since it is shown:

(1) That with a large quantity of lamp black, having a large surface, smaller emulsified droplets of water are obtained in kerosene than when less lamp black is used.

(2) Water wets raw black less readily than it does lamp black having the oils removed by benzene extraction.

(3) Ammonium chloride solution, in normal concentration wets raw lamp black more readily than it does purified black.

(4) Water wets purified lamp black more readily than does ammonium chloride solution, the converse being true of raw black.

(5) As more concentrated solutions of ammonium chloride are used, the emulsified droplets become larger, due to the higher surface tension of the concentrated solution.

(6) The effect of changing the time of mixing is rather indefinite, some tendency being shown for the size of droplets to pass through a minimum as the time is increased.

CLEVELAND, O.

[1] *Loc. cit.*