

Conclusions

The conclusions reached from these preliminary investigations on the refining of active gasolines such as those produced from Colorado oil shale are: (1) that the gum formation may be accelerated by ozone or other oxidizing agents and the gums separated without greatly decreasing the concentration of desirable stable unsaturates in the gasoline; (2) that the oxidation reaction may be very greatly retarded by the addition of phenylhydrazine, thereby stabilizing the gasoline without the removal of the active, gum-forming constituents; and (3) that alcohol might in some instances be added to hold the gums in solution after their formation.

By-products of the investigation are: (1) that ozone may

be used as a qualitative reagent for the detection of those compounds which contain multiple linkages; and (2) that the hastening of the formation of colors and gums by the action of ozone suggests that this material may serve as a reagent for indicating the stability of gasoline in a very rapid and delicate manner.

Literature Cited

- (1) Brooks, "Non-Benzenoid Hydrocarbons," p. 137.
- (2) Brooks, *IND. ENG. CHEM.*, **18**, 1198 (1926).
- (3) Egloff and Morrell, *Ibid.*, **18**, 354 (1926).
- (4) Gurwitsch and Moore, "Scientific Principles of Petroleum Technology," p. 55.
- (5) Richter, "Organic Chemistry," Spielman's translation, pp. 84, 90, and 339.
- (6) Smith and Cooke, U. S. Bur. Mines, *Repts. of Investigations* **2394**.

Solubilities of Oils and Waxes in Organic Solvents^{1,2}

John W. Poole

FUEL AND GAS ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

IT HAS been recognized for many years that certain organic solvents possess the power of selectively dissolving either the paraffin waxes from petroleum lubricants or the lubricants from the waxes. It has furthermore been recognized that solvent extraction might be used to give better separations, and consequently improved products, than does the usual procedure of cold-pressing and sweating (?).

Probably the greatest factors in preventing the use of extraction processes have been high prices of organic solvents and lack of reliable data concerning relative solubilities of wax and oil. However, within recent years the cost of many organic solvents has been greatly reduced and methods of solvent recovery have been improved. The Research Division of Fuel and Gas Engineering has therefore started on a program of securing data having as an object the encouragement of commercial installations for the separation of oil and wax, and the first results of this program are given in this paper.

Previous Work

Sullivan, McGill, and French (6), in investigating the solubility of paraffin wax in midcontinent oils, came to the following important conclusions.

- (1) The solubility of wax in oil increases as the melting point of the wax decreases.
- (2) The solubility of paraffin wax in oil decreases with increasing viscosity of the solvent.
- (3) Difference of solubility due to difference in melting point of wax decreases with decreasing temperature.

¹ Received August 26, 1929.

² This paper covers experimental work done under the direction of the author by R. K. Opper and A. K. Scott and submitted by them in partial fulfillment of the requirements for the degree of bachelor of science from the Massachusetts Institute of Technology. A small amount of supplementary work has been done by the author, while a slightly different arrangement has been made of the data together with somewhat different interpretations. The original data can be found in the thesis, a copy of which is preserved in the Institute Library.

Data concerning the relative solubilities of wax and oil in several organic solvents have been secured for the purpose of encouraging the commercial use of extraction processes for the separation of oils and waxes. The work indicates that of the solvents investigated—acetone, butanol, acetone-butanol mix, ethyl acetate, butyl acetate, chlorobenzene, and toluene—butanol offers the best possibilities for solvent extraction, when one considers selective solvent power, temperature of use, volatility, and initial cost. Addition of acetone does not appear to improve the qualities of butanol. After butanol, ethyl and butyl acetates seem to be the most suitable for commercial applications.

Weber and Dunlap (9), in their investigations of the solubility of paraffin wax in normal pentane, normal hexane, normal heptane, normal octane, and isodecane, quite conclusively substantiated the results of Sullivan, McGill, and French. Their work shows a decided decrease in solubility with increase in molecular weight, indicating more or less that equal mols of solvent dissolve equal quantities of wax, and

suggests the possibility of separation using a close-cut kerosene or heavy naphtha as a selective solvent. In this connection a patent issued to Greenspar (2) states that "kerosene is added to effect crystallization at 27-32° F." The oil is then separated from wax crystals and amorphous wax and kerosene is distilled off until the residue is a high-grade cylinder stock.

Henderson and Ferris (3) found acetone and nitrobenzene to have good selective solvent qualities for oil over wax and on this knowledge developed a method for the determination of paraffin wax in crude wax. A modification of this method, considerably simplified in manipulation, the author has employed satisfactorily on Mexican products.

In a summary of investigations using isopropyl and secondary butyl alcohols and acetone and their mixtures, Smith (5) reported that the constant-boiling mixture of isopropyl alcohol and water has no advantages over acetone but that the alcohol, dehydrated by solid sodium hydroxide and anhydrous copper sulfate, was an excellent solvent. Secondary butyl alcohol was claimed to give good results, as also were certain mixes with acetone. However, the article is of limited value since the data are but vaguely quantitative, and temperatures other than those close to 32° F. (0° C.) were not investigated.

Finally, there are several patents which have a definite bearing on the problem. Wilson (10) separated paraffin wax from mineral oils by treating a thin composition containing such substances with a miscible liquid comprising isopropyl alcohol, which precipitates the bulk of the wax.

A British patent (1) states that trichloroethylene or other

Qualitative Solubility Chart

SOLVENT	BOILING POINT	APPROX. PRICE PER GAL.	10° C.				21° C.				HIGHER TEMPERATURES a, b				REMARKS
			A	B	C	D	A	B	C	D	A	B	C	D	
Ethyl acetate	77	\$1.10	100	-50	100	0	100	-50	100	0	..	100 (68)	..	100 (68)	Apparently has fairly good selective qualities; A and C appear more soluble than B. 1B and 2B separate slowly from solution
Butyl acetate	125	1.40	100	100	100	0	100	100	100	5	100 (50)	Has marked selectivity for oil over wax; ppt. from 1D and 2D somewhat crystalline
Amyl acetate	148	1.60	100	100	100	0	100	100	100	5	100 (51)	Same as for butyl acetate
Kerosene	240-500	0.12	100	100	100	0	100	100	100	5	100 (65)	Same as for butyl acetate
Toluene	111	0.40	100	100	100	0	100	100	100	5	100 (55)	Same as for butyl acetate
Xylene	142	0.40	100	100	100	0	100	100	100	5	100 (50)	Same as for butyl acetate
Turpentine	300	0.60	100	100	100	0	100	100	100	5	100 (51)	Same as for butyl acetate
Chlorobenzene	132	0.64	100	100	100	0	100	100	100	15	100 (65)	Marked selectivity for oil over wax. 1D and 2D very crystalline
Carbon tetrachloride	76	0.90	100	100	100	0	100	100	100	5	100 (65)	A, B, C, and D darken on standing
Tetrachloroethane	135	1.90	100	100	100	0	100	100	100	0	100 (50)	Good selective qualities, but A, B, C, and D darken on standing
Ethylene dichloride	Past experience shows this to possess good selective qualities, but that solutions darken on standing
Ethyl alcohol	78	2.70	0	0	0	0	0	0	0	0	0	0	0	0	Apparently no selective qualities
n-Propyl alcohol	97	1.00	25	15	20	0	25	15	20	0	100 (35)	100 (75)	100 (70)	100 (65)	A appears more soluble than C, and C more than B; selectivity for oil over wax
Isopropyl alcohol	83	1.00	-15	-15	-15	0	-15	-15	-15	0	100 (70)	50 (80)	100 (75)	100 (75)	Seems to have selectivity for oil over wax; oil layer increases
Butanol	117	1.40	100	30	100	0	100	30	100	0	..	100 (80)	..	100 (50)	Apparently has good selective qualities; A and C appear to be more soluble than B
Amyl alcohol	138	1.67	100	100	100	0	100	100	100	5	100 (55)	Apparently has marked selectivity for oil over wax
Diacetone alcohol	...	1.70	0	0	0	0	0	0	0	0	100 (77)	10 (94)	100 (88)	0 (88)	Some selective qualities at high temperatures
Acetone	56	1.00	-10	-10	-10	0	-10	-10	-10	0	0 (87)	0 (87)	0 (87)	0 (87)	Does not appear to have very good selective possibilities
Ethyl methyl ketone	81	2.00	100	-25	100	0	100	-25	100	0	..	100 (57)	..	100 (53)	Apparently has fairly good selective qualities; A and C appear more soluble than B
50% Butanol } 50% Acetone }	100	0	0	0	100	0	0	0	..	0 (82)	100 (82)	100 (60)	Marked selectivity for A over B, C, and D at low temperatures
Mesityl oxide	128	..	100	100	100	0	100	100	100	5	100 (50)	Marked selectivity for oil over wax
n-Butylaldehyde	100	100	100	0	100	100	100	5	100 (50)	Same remarks as for butyl acetate
Acetic anhydride	137	2.61	0	0	0	0	0	0	0	0	0 (90)	0 (90)	0 (85)	0 (50)	Has apparently no selective qualities
Glacial acetic acid	118	1.20	-15	-15	-15	0	-15	-15	-15	0	-15 (92)	-15 (92)	-15 (92)	0 (75)	Has apparently no selective qualities
Dibutyl phthalate	100	0	100	0	100	0	100	0	..	100 (85)	..	100 (60)	A and C seem more soluble than B; apparently has good selective qualities; solvent viscous
Cellosolve	...	2.03	0	0	0	0	0	0	0	0	100 (56)	100 (90)	100 (75)	100 (92)	May have some selective qualities at high temperatures
Methyl Cellosolve	124	1.95	-15	0	-10	0	-15	0	-10	0	-15 (94)	0 (92)	-10 (90)	0 (50)	Apparently no selective qualities
Butyl Cellosolve	134	2.48	100	100	100	0	100	100	100	0	100 (50)	Appears to have good selective qualities; marked selectivity for oil over wax

A—10 cc. Texas oil and 10 cc. solvent; B—10 cc. Pennsylvania oil and 10 cc. solvent; C—5 cc. Texas oil, 5 cc. Pennsylvania oil, and 10 cc. solvent; D—10 cc. melted wax and 10 cc. solvent.

° Numerical values represent the apparent percentage increase or decrease (negative values) in the solvent layer.

† Temperatures are indicated by numbers in parentheses and are in degrees Centigrade.

liquid-making oil heavier than wax is added before centrifugal separation and a U. S. patent (8) states that steam-refined stock is diluted with a solvent (methyl ethyl ketone) in which petrolatum is less soluble than in naphtha and the then diluted stock is chilled to separate petrolatum. A patent (4) issued to Lane in March, 1929, states: "In order to remove petrolatum from oil it is mixed with benzol acetone, cooled, and the waxy material separated."

Experimental Procedure

A large number of solvents was chosen with the view of covering fairly well the different types that are commercially available. These solvents were mixed with an oil (viscosity 300 to 350 seconds at 38° C.) from a Pennsylvania crude, a similar oil from a coastal crude, and a wax melting at 122° F.

(50° C.) (A. S. T. M. Method D-87-22). Solubilities were estimated by inspection at 10° and 21° C., and at some higher temperature as determined by the temperature of complete miscibility, boiling point of solvent, or highest temperature obtainable in the steam bath in which the mixtures were heated. Any peculiarities of action were also noted. These results were tabulated as shown in the accompanying table. Based on the results given in this table six solvents were chosen for exact quantitative determination of solubility at varying temperature.

Discussion of Qualitative Determinations

In the table it will be noted that as the temperature increases the solubility of wax increases faster than the solubility of oils. This seems to be a general fact. Specifically,

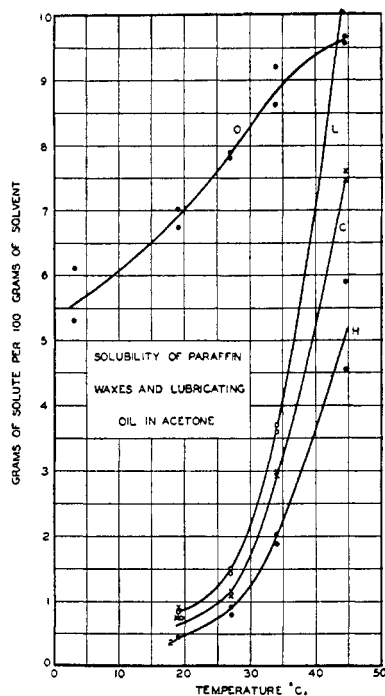


Figure 1

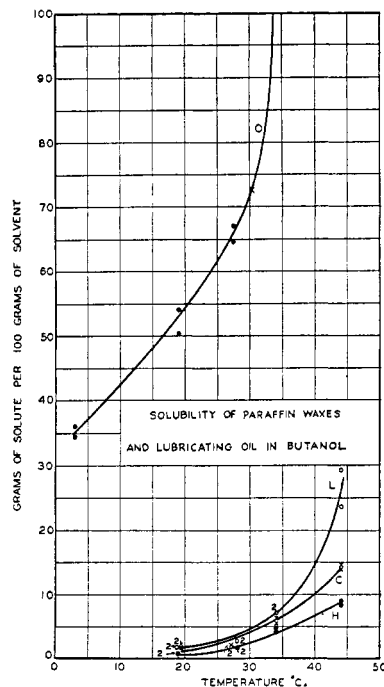


Figure 2

however, there are numerous differences of characteristics, some of which cause the immediate discarding of the solvent as a commercial possibility.

In tetrachloroethane, ethylene dichloride, and carbon tetrachloride the samples darkened on standing—indicating chemical reaction and improbability that the solvent can be of use in this field.

Ethyl alcohol seemed to have practically no solvent power for either wax or oil. The higher alcohols seem better, amyl apparently the best; normal propyl, isopropyl, and butyl

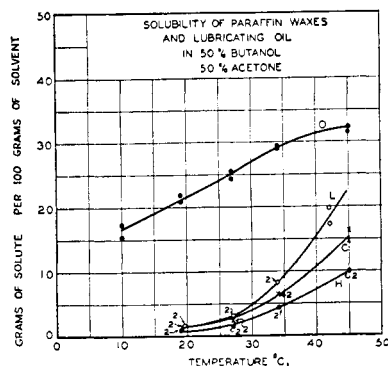


Figure 3

seemed to be between ethyl and amyl alcohols, suggesting that as molecular size increases the solvent power of the alcohols will improve.

Diacetone alcohol seems to possess very good selective powers between 75° and 100° C., and might produce very good results. It should be investigated quantitatively.

Acetone, while showing decided selectivity, dissolves both wax and oil so sparingly as to be rather unattractive.

Chlorobenzene, methyl ethyl ketone, mesityl oxide, normal butylaldehyde, butyl Cellosolve, and ethyl, butyl, and amyl acetates all seem to possess good possibilities as selective solvents, and warrant further investigation.

Kerosene, turpentine, toluene, and xylene also show de-

cidated selectivity, but precipitate gelatinous masses of wax when cooled, that suggest difficulties of separation. However, these solvents might be made to do good work if the problem of wax and solution separation could be met.

Acetic anhydride, glacial acetic acid, and methyl Cellosolve apparently have little selective power. Although careful quantitative investigation of the last two might change this viewpoint, none of the three seems attractive.

Dibutyl phthalate gives indications of being a possibility, but as Pennsylvania base oils are sparingly soluble and the solvent is quite viscous, it does not seem attractive.

Quantitative Determinations

Since the time available for this work was limited, it was necessary to confine the quantitative determinations to those solvents that seemed most likely to give the maximum information. The seven solvents chosen were commercial grades of acetone, butanol, acetone-butanol mixture of equal volumes, chlorobenzene, ethyl acetate, butyl acetate, and toluene.

For solutes were used a 325- to 350-second (Saybolt Universal at 100° F.) paraffin-base oil from Pennsylvania crude and waxes having A. S. T. M. melting points of 50.0°, 53.9°, and 47.3° C. The wax of 50.0° C. was a commercial wax, and the other two were prepared from this commercial wax by four recrystallizations from acetone, each crystallization producing a higher melting and lower melting wax of approximately equal volumes.

All wax melting above 50.0° C. was mixed together to form the 53.9° C. wax and all melting below to form the 47.3° C. wax. Each of the two cuts represented about half of the original volume of the wax from which it was prepared.

A 25-cc. portion of solvent was placed in an 8-inch (20-cm.) test tube, and the solute added in a slight excess. This tube was then placed in a thermostatically controlled bath and allowed to stand overnight. On the following morning the solutions were inspected to make certain of the small excess of solute, after which a sample of approximately 5 cc. was blown from the test tube into a tared weighing bottle and weighed. This bottle was then placed on a steam bath and the solvent evaporated to constant weight under an air jet. The quantity of solvent was then determined by difference.

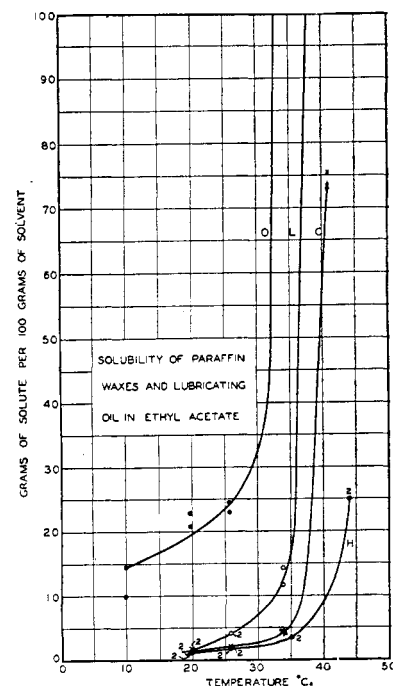


Figure 4

In each case two determinations were made which, with the exception of certain of the points of extremely low solubility, checked within 5 per cent. The points were averaged by drawing smooth curves of temperature *vs.* solubility through these points. (Figures 1 to 7)

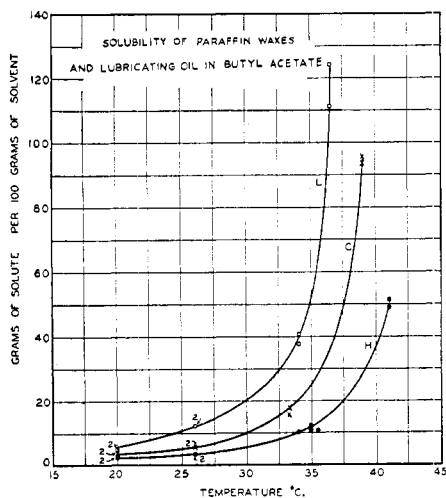


Figure 5

Discussion of Temperature-Solubility Curves

ACETONE—Although showing a much higher solubility for oil than for wax (Figure 1), acetone is so poor a solvent for either that its use for extracting oil from an oil-wax mixture is very unlikely. Very large volumes of liquid would be required—a matter which will probably limit its use to laboratory work. Since hydrocarbons are so sparingly soluble, these data have been plotted on a much larger scale than was used for the other solvents. Inspection of the four curves also shows that, whereas the solubility of oil and wax increases steadily with temperatures above 30° C., the solubility of wax increases much faster than that of oil, and probably the two would eventually become equal at some temperature around 50° C. More data should be obtained between 45° and 50° C. in order to make certain about this critical point.

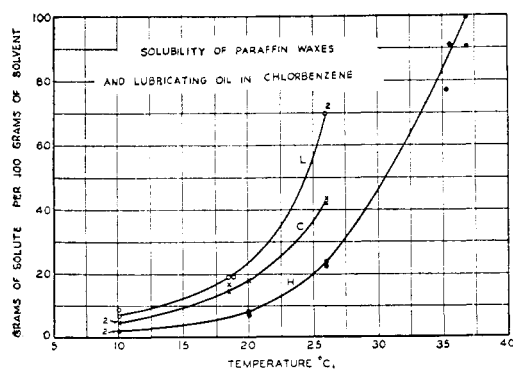


Figure 6

BUTANOL—From Figure 2 it is quite evident that butanol has exceptionally good selective powers. Just below 30° C. oil appears to be completely miscible in butanol, while even as low as 0° C. butanol dissolves practically one-third its weight of oil. On the other hand, up to about 25° C. the solubility of wax in butanol is below 2 per cent and even at 30° C., the point of complete miscibility of oil, the solubility of wax seems to be less than 4 per cent. Like the

other solvents, however, there comes a temperature (about 35° C.) where the solubility of wax also increases very fast and, as is shown by the qualitative work, at 50° C. has reached the point of complete miscibility. The paraffin-base oil is completely miscible at 34° C.

BUTANOL-ACETONE (50:50) MIXTURE—The results of the work on this mixture (Figure 3) indicate no advantage over butanol. The curve for oil shows approximately a solubility three times that of acetone, but still a capacity so low as to necessitate very large volumes of solvent.

The wax curves are nearly the same as those for pure butanol—i. e., showing twice the solubility in acetone. Logically it would appear, then, that considerable efficiency would be lost by adding acetone to butanol, since the selectivity is decreased, oil being less soluble than in pure butanol while the solubility of the wax has not been lowered.

ETHYL ACETATE—Ethyl acetate shows a very good selective action for oil over wax. (Figure 4) Except for the fact that up to 25–30° C. oil is considerably less soluble than in butanol, and that the decided increase in the solubility of waxes comes at a lower temperature than for butanol, the characteristics of these two solvents are quite similar. The data indicate that the two solvents would give identical effects at around 30° C. At this point the oil appears to be completely miscible while the solubility of the waxes is still

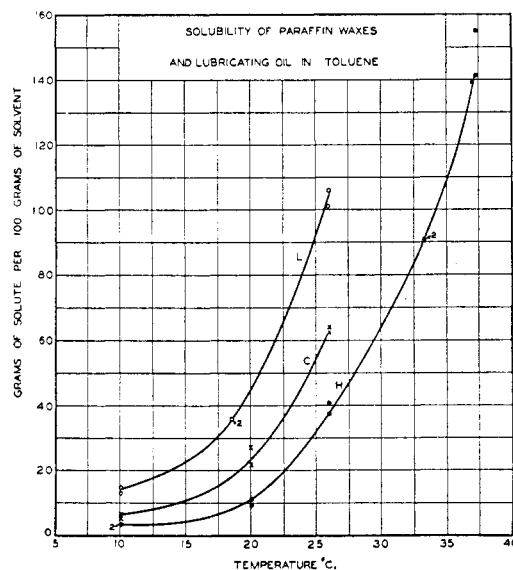


Figure 7

quite low. However, with this solvent the point of complete miscibility of oil is much closer to the point where the solubility of waxes also becomes extremely high than it is in the case of butanol. Furthermore, there seems to be a much greater variance of the point where the waxes increase greatly in solubility, a certain lowering of the melting point apparently causing the curve to break upward at a much lower temperature than would be true with butanol, which phenomenon might cause the very low melting waxes to be dissolved in inconveniently large quantities at what might seem to be the most desirable working temperature.

BUTYL ACETATE, CHLOROBENZENE, TOLUENE—Figures 5, 6, and 7 show the temperature-solubility curves for these three solvents. All three are completely miscible with oil over the range under consideration. All three sets of curves for wax are similar in shape, although there is a considerable difference in the respective solvent powers below 30° C. Except for butyl acetate, the solubilities at these points are

so great that there appears to be little possibility of these solvents entering seriously into our field of interest. The butyl acetate might be a possibility and, showing as it does its greatest selectivity below 20° C., might under special conditions prove to be the most satisfactory solvent.

In interpreting the foregoing data it should be remembered that determinations of both oil and wax were made with only one of these constituents present in the solvent. Without doubt a mixture in which both a solvent of high selectivity and oil are present will have a greater solvent power for wax than will the pure solvent. Data of such a nature are, of course, essential to the proper development of a commercial extraction method. The securing of these data is

the next step which should be made toward the completion of this work.

Literature Cited

- (1) Aktiebolaget Separator-Nobel, British Patent 276,658 (August 24, 1926).
- (2) Greenspar, U. S. Patent 1,562,425 (November 17, 1925).
- (3) Henderson and Ferris, *IND. ENG. CHEM.*, **19**, 2624 (1927).
- (4) Lane, U. S. Patent 1,706,120 (March 19, 1929).
- (5) Smith, *Oil Gas J.*, **26**, No. 17, 146 (1928).
- (6) Sullivan, McGill, and French, *IND. ENG. CHEM.*, **19**, 1042 (1927).
- (7) Truesdell, *Nat. Petroleum News*, **20**, No. 6, 22 (1928).
- (8) Wagner, U. S. Patent 1,869,151 (May 8, 1928).
- (9) Weber and Dunlap, *Nat. Petroleum News*, **20**, 383 (1928).
- (10) Wilson, Canadian Patent 269,444 (April 5, 1927).
- (11) Wyant and Marsh, *Bur. Mines, Tech. Paper* **368** (1925).

Adhesion Tension Values of Different Types of Carbon Black against Water and against Benzene¹

F. E. Bartell and Carleton N. Smith

UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.

COMMERCIAL carbon blacks from different sources exhibit widely different properties. Numerous attempts have been made to account for the diversity in properties of such carbons. The seemingly more plausible theories attribute the diversity to differences in (a) crystal structure, (b) effective surface area, and (c) "activity." The third factor is, however, largely dependent upon either or both of the others.

X-ray studies have contributed much to our information concerning crystal structure of the different modifications of carbon. The diamond and graphite are generally accepted as being structurally distinctive forms. Opinions differ as to the structure of the so-called amorphous or microcrystalline form (14), though much of the evidence points to a definite crystalline structure for it (1). Microcrystalline carbon may, according to some investigators, appear in more than one form—as, for example, alpha and beta modifications (7).

Effective surface area of carbon depends not only upon the degree of subdivision, which may be regulated by soot deposition or by grinding and dispersion of massive carbon, but also upon the degree of surface roughening, as by pitting, etc., or upon the number and size of micropores which may be present.

The high "activity" of certain carbons has been attributed (1) to crystal structure, (2) to specific (effective) surface area, and (3) to the presence of impurities. It has been found (13) that ash-free graphite adsorbs succinic acid but leaves methylene blue untouched. Diamond powder adsorbs in the reverse order. Carbon black (methane soot) behaves like diamond, and activated anthracite like graphite. It thus appears that the precise crystal structure of a solid is important in determining its activity. The work of Miller (12) has gone far to prove that activation of carbon does

Adhesion tension values have been determined for seven different types of carbon black against water and against benzene. The carbons were subjected to heat treatment and evacuation. It was found that reliable data could be obtained only when the carbon particles were so large that compressed membranes of them had pore radii greater than (approximately) 2×10^{-6} cm.

It has been shown beyond reasonable doubt that different commercial carbon blacks possess different adhesion tension values against water and against benzene, and that heat treatment alters the adhesion tension of these carbons against different liquids.

not necessarily require the presence of impurities, as has often been maintained. On the contrary, it has been shown (5) that the presence of "impurities" on the surface tends rather to decrease the adsorptive capacity of carbon for other substances, inasmuch as the already adsorbed impurity has used up part of the adsorption surface. The conclusion

seems justified that activity is largely a function of surface area. This view has been further substantiated by work in this laboratory on heat of wetting of carbon by binary liquid mixtures (3). Recent unpublished work on adsorption by Bartell and Miller has shown that a direct relationship exists between adhesion tension and adsorption when a given solid is used with different liquids. Adhesion tension may be considered to represent the degree of wetting of a solid by a liquid (2, 4). It is a measure of the change in free surface energy per unit area which occurs when a solid against air (or gas) interface is replaced by a solid against liquid interface. It is numerically equal to the difference between the surface tension of the solid, S_1 , and the interfacial tension solid against liquid, S_{12} , and may be expressed by the equation:

$$A = S_1 - S_{12}$$

Since the adhesion tension is a measure of the change of free surface energy per unit area which occurs when a solid surface is wetted by a liquid, determination of adhesion tension alone cannot serve to determine the fundamental difference between two carbons of different activity.

If, however, adhesion tension values were obtained for a series of different carbons against several different liquids, one might have good evidence as to whether the difference in the adhesion tension values were due to differences in crystal structure or to the presence of adsorbed impurities. In case the differences were due to crystal structure, a uniform difference in the adhesion tension values might be expected for a given series of carbons against each of different liquids. If, on the other hand, the differences were due to adsorbed impurities, less of uniformity in the ad-

¹ Received July 29, 1929.

² From a dissertation submitted by Carleton N. Smith to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of doctor of philosophy, 1929.