

<sup>3</sup> Obtained from distillation of bitumens: This includes petroleum pitch, either "straight" or "cut back."

<sup>4</sup> Obtained from the "oxidation" of bitumens: This includes "blown" petroleum pitches.

<sup>5</sup> Obtained from the "sulfurization" of bitumens: This includes the so-called "Dubb's asphalt," obtained by heating petroleum residues with sulfur.

<sup>6</sup> Variable Origin: It may be of animal, vegetable or mineral origin and includes both natural and artificial products.

<sup>7</sup> Hydrocarbon Complex: Often contains oxygen, nitrogen or sulfur derivatives of the hydrocarbons. This excludes vegetable resins, vegetable and animal waxes, etc.

<sup>8</sup> Associated with a mineral matrix: This may be calcareous, siliceous, earthy, etc., which is usually present as an impurity.

<sup>9</sup> Solutions in essential oils: The essential oils consisting of terpenes.

<sup>10</sup> Variable Compositions: No exact chemical composition. Usually mixtures of closely related substances, composed of the elements carbon and hydrogen, together with varying amounts of oxygen, sulfur and nitrogen. May contain hydrocarbons, fats, fatty acids, resin acids, waxes, etc., etc., or mixtures of these.

<sup>11</sup> Insoluble in water: This excludes gum resins, carbohydrates, etc.

<sup>12</sup> Partly soluble in water: The carbohydrates ("gums") are the soluble constituents.

<sup>13</sup> Soluble in carbon disulfide, benzol, etc.: This does not take into consideration the mineral constituents present and excludes the pyro bitumens.

<sup>14</sup> Relatively insoluble in carbon disulfide, benzol, etc.: This likewise does not take into consideration the mineral constituents present and excludes the bitumens proper, tars, and most pitches.

<sup>15</sup> Viscous: This excludes gaseous and solid bitumens.

<sup>16</sup> Viscous to semi-solid: This is governed by the amount of essential oil present.

<sup>17</sup> Viscous to solid: Some occur as sticky masses, others as hard and brittle solids at ordinary temperatures. Plasticity is an inherent or an acquired property. Some are plastic at ordinary temperatures, others become plastic, under the influence of heat or when combined with suitable fluxes. This excludes the gaseous and liquid bitumens, tars and oleo resins.

<sup>18</sup> Viscous to solid Bitumens and Pyro Bitumens: This includes the hard and relatively insoluble wood-tar pitches, etc.

<sup>19</sup> Semi-solid to solid: Usually contains small amounts of essential oils, which govern the consistency.

<sup>20</sup> Solid: This excludes gaseous, liquid and viscous substances.

<sup>21</sup> Variable Hardness: This includes gaseous (in the case of bitumens), also liquid, viscous and solid substances.

<sup>22</sup> Light Colored in Mass: This excludes the mineral resins.

<sup>23</sup> Dark Colored in Mass: Usually black. This excludes paraffin (ceresine), and vegetable resins.

<sup>24</sup> Variable Color in Mass: Color ranges from pure white (paraffin wax), to very dark, almost black (ozokerite and montan wax).

<sup>25</sup> Amorphous Structure: In distinction to crystalline.

<sup>26</sup> Conchoidal Fracture: But sometimes "hackly."

<sup>27</sup> Waxy Lustre: Mineral waxes have a waxy lustre, and are, therefore, included.

<sup>28</sup> Resinous Lustre: This together with the light color is characteristic of the true resins.

<sup>29</sup> Non-adherent to slightly adherent feel: In distinction to the unctuous feel of waxes.

<sup>30</sup> Uctuous Feel: This is characteristic of waxes.

<sup>31</sup> Tarry Odor: Most tars have a characteristic odor, but some mineral tars (*e. g.*, maltha, petroleum tars, etc.) are practically free from odor.

<sup>32</sup> Extremely susceptible to changes in temperature: Meaning that they pass rapidly from the solid to the liquid state as the temperature is raised (*i. e.*, have a high "susceptibility factor").

<sup>33</sup> Fusible: Soften on warming, melt *without* decomposition, decompose as the temperature is increased, and finally burn with a smoky flame, leaving a carbonaceous residue behind. This excludes the asphaltites, as these are difficultly fusible, and the pyro bitumens as these are infusible (but which, however, decompose and melt at higher temperatures).

<sup>34</sup> Difficultly Fusible: Intermediate between the natural asphalts and pyro bitumens.

<sup>35</sup> Infusible: This excludes the bitumens proper, vegetable resins, tars, pitches, etc.

The chart on page 14 shows the relation between bituminous substances, bitumens, pyro bitumens, maltha, asphaltum, asphaltite, tars and pitches; also between resinous substances, true resins, oleo resins, gum resins and mineral resins.

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## THE EFFECT OF EXPOSURE ON BITUMENS<sup>1</sup>

By PRÉVOST HUBBARD AND C. S. REEVE

It is a well known fact that in all types of bitumens changes occur upon aging and exposure. These changes often result in noticeable variations in characteristics which are at least qualitatively apparent to the casual observer. They may be the result of purely physical phenomena or of chemical reactions which take place either between certain inherent constituents of the bitumens themselves or between the bitumens and some external agent. Thus loss of the lighter oils by volatilization may be considered a purely physical cause of change while molecular rearrangements, inter-reactions and the oxidation of certain constituents are examples of chemical changes.

The object of our investigation was to determine the nature of changes due to exposure which take place in various types of bitumens, particularly those used in the treatment and construction of roads and pavements. At the outset it was realized that to exactly duplicate service conditions in a laboratory test would be impracticable if not impossible but an attempt was made to approach these conditions as nearly as possible. Eight samples of bituminous road materials were selected for the following experiments as representing the principal types in common use. The results of the usual examination of these materials are given below. These and all other analyses reported in this paper were made according to methods which we have published<sup>2</sup> elsewhere and which, therefore, need not be described here.

The form of box in which the exposures were made is shown in Fig. I. This box was made of  $\frac{3}{4}$  inch wood, and its interior dimensions were  $25 \times 14\frac{1}{2} \times$

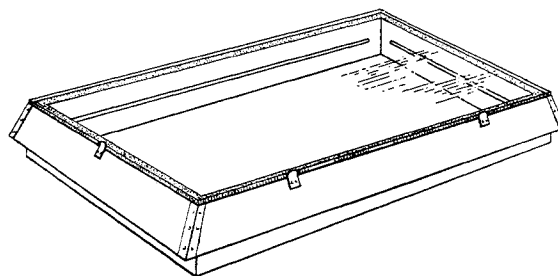


FIG. I.—EXPOSURE BOX

2 inches. A felt rim surrounded the upper edge and upon this rested a  $\frac{1}{4}$  inch plate-glass cover. To provide for some circulation of air, a  $\frac{1}{4}$  inch slot was cut through each of the sides as shown in the sketch, and a thin board extended from the upper edge at an angle of about  $45^\circ$  to prevent dust and rain from entering through the slot.

At first strips of cheese-cloth were stretched between the bottom and the edge of the slanting side board, but when it was found that this did not insure perfect freedom from dust, cotton batting was loosely packed beneath the slanting board and against the

<sup>1</sup> Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

<sup>2</sup> Bull. 38, Office of Public Roads, U. S. Department of Agriculture.

ventilating slot. This successfully excluded dust and permitted a fair circulation of air.

The samples were placed in Syracuse watch glasses, as shown in the illustration (Fig. II). The depressions in these glasses are approximately 47 mm. in diameter, by 8 mm. deep, and they were filled to a uniform depth of 32 mm. with each of the materials to be exposed. The samples were melted and thoroughly stirred, and each set of specimens was made at one pouring, the depth of bitumen being obtained by means of a gauge immersed in it.

The several types of material selected and their characteristics are shown in the following tables:

TABLE I—OIL AND ASPHALT PRODUCTS

|                                       | Fluxed Bermudez asphalt | Gilsonite oil asphalt | Oil asphalt      | Semi-asphaltic petroleum residuum | California petroleum residuum |
|---------------------------------------|-------------------------|-----------------------|------------------|-----------------------------------|-------------------------------|
| Specific gravity 25° C./25° C.        | 1.040                   | 0.958                 | 0.985            | 0.936                             | 0.998                         |
| Consistency                           | 51 <sup>1</sup>         | 243 <sup>1</sup>      | 228 <sup>1</sup> | 31.22                             | 8' 8" <sup>2</sup>            |
| % Loss 163° C., 5 hours               | ..                      | 1.71                  | 0.43             | 3.75                              | 0.49                          |
| Consistency of residue                | ..                      | 184 <sup>1</sup>      | 137 <sup>1</sup> | fluid                             | 12' 1" <sup>2</sup>           |
| Bitumen soluble in CS <sub>2</sub>    | 96.43                   | 99.67                 | 99.70            | 99.96                             | 99.88                         |
| Organic matter insoluble              | 1.62                    | 0.13                  | 0.19             | 0.02                              | 0.08                          |
| Inorganic matter insoluble            | 1.95                    | 0.20                  | 0.11             | 0.02                              | 0.04                          |
| % Bitumen insoluble in 86° B. naphtha | 25.16                   | 22.16                 | 20.27            | 1.93                              | 6.57                          |
| % Fixed carbon                        | 12.10                   | 8.87                  | 11.98            | 4.07                              | 5.67                          |

<sup>1</sup> Penetration 100 g., 5 sec., 25° C.

<sup>2</sup> Specific viscosity (Engler) 50° C.

<sup>3</sup> Float test 32° C.

TABLE II—TAR PRODUCTS

|                                       | Refined coal tar  | Refined water-gas tar | Refined mixed coal and water-gas tar |
|---------------------------------------|-------------------|-----------------------|--------------------------------------|
| Specific gravity 25° C./25° C.        | 1.227             | 1.174                 | 1.240                                |
| Float test 50° C.                     | 1' 54"            | 2' 38"                | 5' 0"                                |
| % Free carbon                         | 17.31             | 0.60                  | 15.80                                |
| Distillation (by weight) <sup>1</sup> | ..                | ..                    | ..                                   |
| Light oils to 110° C.                 | 0.1               | 0.4 <sup>4</sup>      | ..                                   |
| 2nd Light oils 110° C.-170° C.        | 0.6 <sup>2</sup>  | 0.4 <sup>5</sup>      | ..                                   |
| Dead oils 170° C.-270° C.             | 21.5 <sup>3</sup> | 17.8 <sup>3</sup>     | ..                                   |
| Pitch residue                         | 77.3              | 81.4                  | ..                                   |

<sup>1</sup> 250 cc. sample, 750 cc. glass retort, bottom of thermometer bulb level with bottom juncture of stem and body of retort. Method since discontinued.

<sup>2</sup> 9/10 solid.

<sup>3</sup> 1/4 solid.

<sup>4</sup> Clear.

<sup>5</sup> Slightly cloudy.

<sup>6</sup> Not sufficient sample for distillation.

Six rows, each of which contained one set of the samples, were placed lengthwise of the box. The box was then set with its length east and west outside a window having an open southern exposure.

of comparison with the original analyses. The watch glasses and their contents were first weighed for the purpose of determining any change in weight since placing them in the box. The changes in weight were found to be so slight at this time that no other tests were made. At the end of two months another set of samples was removed and weighed. Owing to cold winter weather the changes in weight were still very small but in general somewhat greater than at the end of one month. At this time, after melting and thorough stirring, portions of each sample were, if sufficiently hard, subjected to the penetration test at 25° C. If too soft for the penetration test a float test was made at 40° C.

The relative degree of hardening due to exposure for this period of time was thus determined. Solubility determinations were then made on another portion of each sample. For the petroleum and asphalt products, 86° B. paraffin naphtha was used as a solvent while c. p. carbon disulfide was used for the tar products. The solutions were filtered through a Gooch crucible fitted with an asbestos pad and the insoluble organic matter determined by weighing the residue before and after ignition. The organic matter insoluble in naphtha was determined on the basis of total bitumen.

All of these tests were repeated at the end of four, six, eight and twelve months' exposure. The results thus obtained are given in the following tables. At the end of each period the general appearance of the samples was noted as described later. At the end of the twelve-month period, a set of samples were photographed for the purpose of showing the very marked differences in the surface appearance of the various bitumens due to exposure. In order to assure ourselves that accumulations of dust could not be held responsible for gain in insoluble organic matter, a large number of determinations of the organic material insoluble in carbon disulfide was made at different periods on the oil and asphalt products. In no case, however, was any appreciable gain to be detected as compared with the original determinations.

In reviewing Table III, it will be noted that the tests were begun during midwinter when changes due to loss by volatilization should be at a minimum. At the end of one month it was found that only the tars and the fluid semi-asphaltic petroleum residuum

TABLE III—CHANGES IN WEIGHT AND CONSISTENCY

|                                   | Dec. 9   |        | Jan. 9  |       | Feb. 9   |       | April 9  |       | June 9   |         | Aug. 9   |     | Dec. 9    |        |
|-----------------------------------|----------|--------|---------|-------|----------|-------|----------|-------|----------|---------|----------|-----|-----------|--------|
|                                   | Original |        | 1 month |       | 2 months |       | 4 months |       | 6 months |         | 8 months |     | 12 months |        |
|                                   | Pen      | Float  | % Wt.   | Pen   | % Wt.    | Pen   | Float    | % Wt. | Pen      | Float   | % Wt.    | Pen | % Wt.     | Pen    |
| Fluxed Bermudez asphalt           | 51       | ..     | +0.05   | ..    | +0.08    | 43    | ..       | +0.14 | 36       | ..      | -0.34    | 26  | ..        | -1.37  |
| Gilsonite—oil asphalt             | 243      | ..     | +0.06   | ..    | +0.09    | 219   | ..       | +0.47 | 203      | ..      | +0.09    | 139 | ..        | -0.86  |
| Oil asphalt                       | 228      | ..     | +0.04   | ..    | +0.10    | 184   | ..       | +0.35 | 164      | ..      | +0.81    | 82  | ..        | +0.92  |
| Semi-asphaltic petroleum residuum | fluid    | ..     | -0.30   | fluid | -0.26    | fluid | ..       | ..    | ..       | ..      | ..       | ..  | ..        | ..     |
| California petroleum residuum     | ..       | 3' 43" | +0.08   | ..    | +0.13    | ..    | 4' 30"   | +0.98 | ..       | 5' 8"   | +1.48    | ..  | 15' 5"    | +2.25  |
| Refined coal tar                  | ..       | 3' 46" | -0.25   | ..    | -0.25    | ..    | 4' 22"   | -3.04 | ..       | 14' 12" | -8.52    | 16  | ..        | -9.58  |
| Refined water-gas tar             | ..       | 5' 14" | -0.11   | ..    | -0.07    | ..    | 6' 58"   | -2.59 | ..       | 18' 48" | -9.54    | 9   | ..        | -11.06 |
| Refined mixed tar                 | 128      | ..     | -0.05   | ..    | -0.02    | 124   | ..       | -1.05 | 89       | ..      | -5.05    | 19  | ..        | -6.00  |

After exposing these samples for a period of one month an entire set was removed from the exposure box and subjected to certain tests for the purpose

had suffered any loss by volatilization and as would be expected these losses were very small. All of the other materials showed a slight gain in weight. At

the end of two months approximately the same situation prevailed although the samples which had previously gained in weight showed a slight additional gain. All of the materials had become somewhat harder with the exception of the refined mixed tar and the semi-asphaltic petroleum residuum which latter was too fluid to permit of a penetration or float determination being made. In the early part of April at the end of four months, the loss in weight

though in tars such loss is probably responsible to a considerable degree for the hardening of these products. The hardening of petroleum and asphalt products is undoubtedly due to oxidation which proceeds slowly at comparatively low temperatures but increases at higher temperatures. It seems probable that oxidation also plays a part in the hardening of tars although the preceding data does not absolutely prove this fact.

TABLE IV—PERCENTAGE GAIN IN INSOLUBLE ORGANIC MATTER

|  | 2 months                              |        |            | 4 months |            | 6 months |            | 8 months |            | 12 months |            |
|--|---------------------------------------|--------|------------|----------|------------|----------|------------|----------|------------|-----------|------------|
|  | Insoluble in 86° B. Petroleum Naphtha |        |            |          |            |          |            |          |            |           |            |
|  | Original                              | Actual | Calculated | Actual   | Calculated | Actual   | Calculated | Actual   | Calculated | Actual    | Calculated |
| Fluxed Bermudez asphalt.....           | 25.16                                 | 0.65   | —0.02      | 1.34     | —0.05      | 4.50     | 0.09       | 7.24     | 0.15       | 9.42      | 0.35       |
| Gilsonite—oil asphalt.....             | 22.42                                 | 0.53   | —0.02      | 1.18     | —0.09      | 2.68     | —0.02      | 3.57     | —0.13      | 4.07      | 0.19       |
| Oil asphalt.....                       | 20.27                                 | 0.30   | —0.02      | 0.54     | —0.07      | 4.33     | —0.16      | 6.13     | —0.38      | 6.10      | —0.19      |
| Semi-asphaltic petroleum residuum..... | 1.93                                  | 1.42   | 0.01       | 3.06     | ...        | 6.24     | ...        | ...      | ...        | ...       | ...        |
| California petroleum residuum.....     | 6.57                                  | 0.88   | —0.01      | 2.53     | —0.07      | 9.78     | —0.10      | 12.35    | —0.15      | 12.96     | —0.12      |
|  | Insoluble in Carbon Disulfide         |        |            |          |            |          |            |          |            |           |            |
| Refined coal tar.....                  | 17.31                                 | 0.82   | 0.04       | 1.93     | 0.54       | 4.64     | 1.61       | 6.34     | 1.83       | 6.42      | 1.87       |
| Refined water-gas tar.....             | 0.60                                  | 0.27   | 0.00       | 0.75     | 0.02       | 2.61     | 0.06       | 3.80     | 0.07       | 4.08      | 0.08       |
| Refined mixed tar.....                 | 15.80                                 | 0.67   | 0.00       | 1.08     | 0.17       | 3.70     | 0.84       | 5.53     | 1.01       | 5.26      | 1.01       |

of the tar samples was quite appreciable running from about 1 to 3 per cent. The petroleum and asphalt products, however, showed a continued increase in weight. At this time it was found that all of the semi-asphaltic petroleum samples had crept over the edge of the watch glasses so that accurate weight determinations could not be made upon them from then on. All of the other materials showed a continued increase in hardness which increase persisted throughout the entire test.

Just before the withdrawal of the samples for the tests at this period, the weather suddenly became warm for several days, and there was an immediate formation of an oily layer upon the lower side of the glass cover. This rapidly increased and after a short time became a thin, hard varnish-like crust which adhered firmly to the glass. Upon attempting to remove it, it was found to be very sparingly soluble in either carbon disulfide or benzol. It was found to be partially soluble in 95 per cent. alcohol with the production of an amber colored solution, and a brownish, insoluble powder. From contemporaneous investigations we have found this to be produced principally as an alteration production of the volatile portion of the tars.

At the end of six months the fluxed Bermudez asphalt was found to have slightly decreased in weight. The petroleum products, however, showed a notable increase in weight, particularly the California residuum. The same was apparent at the end of 8 months at which time, due to warm weather, the loss in weight of the tar samples had almost reached a maximum for the entire 12 months' test. At the end of one year only the California residuum and oil asphalt showed an increase in weight. All of the products were sufficiently hard to permit of penetration determinations being made.

It is apparent from these results that the hardening of all bitumens upon exposure is not due to loss by volatilization of the lighter constituents, alone, al-

In Table IV, the percentage increase in insoluble organic matter of the eight materials at different periods of exposure is given together with the calculated increase or decrease based upon their loss or gain in weight at these periods. As previously stated, 86° B. paraffin naphtha was used as a solvent for the oil and asphalt products while c. p. carbon disulfide was employed for the tar products. This table need not be discussed in detail as practically all of the results show that exposure causes an increase in insoluble organic material which is considerably in excess of the increases calculated from their loss by volatilization. As compared with Table III it is apparent that this increase in insoluble material accompanies the increase in hardness and from what is known of the behavior of oil and asphalt products, upon being blown it would seem reasonable to suppose that such insoluble materials are the direct products of oxidation. Such products may actually contain oxygen or they may be the result of nucleus condensation brought about by the reaction of oxygen with two or more hydrocarbons originally present in the bitumens.

The increase in material insoluble in carbon disulfide for the tar samples may also have been caused by oxidation or molecular rearrangements and inter-reactions between certain constituents of the tar. That the latter type of reaction probably occurs to some extent has been shown by us in a recent paper.<sup>1</sup> It is believed that these results clearly demonstrate that so called "free carbon" is actually formed in tars upon exposure.

While the surface of all of the materials was smooth and glossy when first placed in the watch glasses considerable differences in their surface appearance and condition were apparent at different periods of exposure. Fig. II shows a photograph of the materials at the end of twelve months. At this time the observations given below Fig. II were made.

<sup>1</sup> *Proc. Am. Soc. for Testing Materials*, **11**, 666 (1911).

In conclusion it should be stated that while the above results show interesting differences in the effect

in tending to change or modify the results obtained in the above described research.

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#### EXAMPLES OF THE EFFICIENCY OF CALCIUM HYPOCHLORITE IN TREATING TURBID WATERS<sup>1</sup>

By EDWARD BARTOW

We have recently had the privilege of noting the action of calcium hypochlorite in the purification of turbid waters in some of the plants in the North Central United States. Results from two of the plants illustrate in different ways the efficiency of the chemical. In one case the chemical was added at the end of a long sedimentation period, during which some reduction had taken place. The chemical reduced the number of bacteria very materially, and filtration was able to effect a still greater reduction. In the other case, owing to failure to receive a shipment of the chemical, none could be used for six days. There was at once a decided increase in the number of bacteria, followed by a decrease when the chemical was again applied even though the water, as shown by the turbidity, was the worst for years.

The results obtained in the first case are shown in Table I. The colony counts were obtained on gelatine at 20° C. The water treated was from the Mississippi River.

The number of colonies in the raw water is shown in the first column. The number of colonies in the effluent from a settling basin of twenty-four hours' capacity is shown in the second column. As a rule, the number was reduced. The average reduction was 65 per cent. The number of colonies in the water after treatment with calcium hypochlorite and approximately one and one-half hours additional sedimentation is shown in the third column. The number of colonies was further reduced 97.6 per cent. or 99.1 per cent. from the number in the raw water. The number of colonies obtained from the water after filtration is shown in the fourth column. There was a further reduction of 82 per cent. or a total bacterial removal of 99.8 per cent.

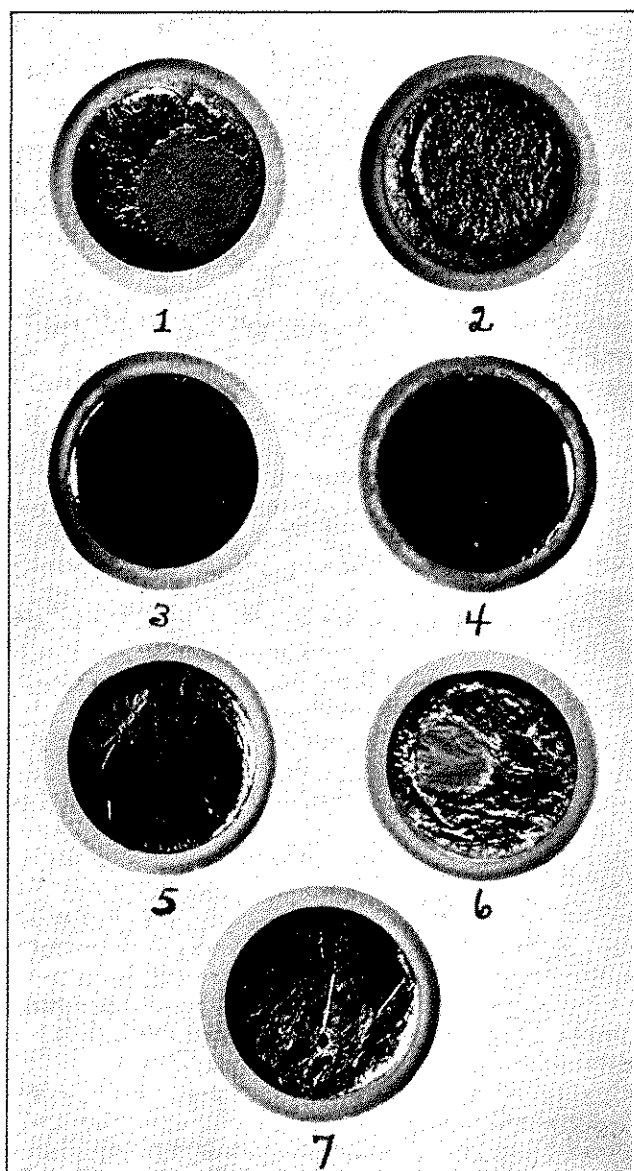


FIG. II—BITUMENS AFTER 12 MONTHS' EXPOSURE

1. Fluxed Bermudez Asphalt: Portion of surface glossy and dark brown, showing an enclosed patch of about 1 inch diameter, dull and light brown.
2. Gilsonite Oil Asphalt: Surface bright but rough and granular.
3. Oil Asphalt: Smooth, bright, glossy surface.
4. California Petroleum Residuum: Smooth surface, glossy and sticky.
5. Refined Coal Tar: Surface drawn and cracked in places. Surface black; streak brown.
6. Refined Water Gas Tar: Surface wrinkled and showing large brown patch of about 1/2 inch diameter. General crystalline appearance.
7. Refined Mixed Tar: Surface drawn and cracked. Friable black film; streak brown.

of exposure upon characteristic types of bituminous materials, they should not, for practical purposes, be too positively or rigidly interpreted. When these materials are exposed to an actual service test in connection with the particular purpose for which they are to be used, other factors undoubtedly play a part

TABLE I—COLONIES GROWING ON GELATINE AT 20° C. IN 48 HOURS

| Date                | Raw    | After sedimentation | After hypochlorite | Filter effluent |
|---------------------|--------|---------------------|--------------------|-----------------|
| Oct. 17, 1910.....  | 28,000 | 9,700               | 95                 | 75              |
| Nov. 23, 1910.....  | 2,300  | 2,200               | 47                 | 17              |
| Dec. 18, 1910.....  | 5,600  | 1,200               | 70                 | 31              |
| Feb. 6, 1911.....   | 46,500 | 11,000              | 690                | 44              |
| May 4, 1911.....    | 26,500 | 3,300               | 370                | 40              |
| Aug. 15, 1911.....  | 13,000 | 280                 | 50                 | 8               |
| Sept. 12, 1911..... | 19,000 | 5,000               | 37                 | 17              |
| Oct. 18, 1911.....  | 5,400  | 2,800               | 170                | 72              |
| Jan. 25, 1912.....  | 500    | 17,000              | 45                 | 12              |
| Mar. 29, 1912.....  | 67,000 | 22,000              | 260                | 10              |
| Average, 21,380     |        | 7,448               | 183                | 33              |

Tests for gas forming bacteria were made on the same samples of water and the results correspond very well with the reduction in the number of bacteria.

<sup>1</sup> Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.