

# Effect of Chlorination on Oxidizability of Road Asphalts

FREDERICK C. SANDERSON, Assistant Professor of Civil Engineering  
Yale University

Oxidation of the asphaltic binder in bituminous pavements is a frequent cause of pavement failure. The hardening, or loss of penetration of the asphalt which results from oxidation occurs gradually over the life span of the pavement. It can also take place fairly rapidly at the elevated temperatures used during mixing operations.

This paper describes some of the physical and chemical effects of direct chlorination on road building asphalts. In the laboratory, experimental data have been obtained which indicate that the oxidizability of the asphalt may be materially reduced by treatment with chlorine.

The action of chlorine on asphalt is in many respects similar to that of oxygen. However, it is to be expected that the loss of penetration resulting from treatment with limited amounts of chlorine will be less than that resulting from a chemically comparable amount of oxidation. Because of the fact that chlorine is in general more active chemically than oxygen, it is also to be expected that the compounds formed in asphalt by treatment with chlorine will be relatively stable and that the resistance of the asphalt to oxidation will be increased.

In the laboratory, eight samples of asphalt cement were subjected to direct chlorination. Tests performed on the samples before and after chlorination, including the Anderson-Stross-Ellings tests, indicate that although the penetration of the asphalt cements tested is decreased by chlorination, the resistance to hardening is greatly increased.

● **FAILURES** of asphalt pavements other than those resulting from poor subgrade conditions or faulty pavement design appear to be due primarily to one of two causes; stripping, or hardening of the asphalt.

Loss of penetration or hardening occurs gradually by weathering over the life span of the pavement. It can also take place fairly rapidly at the elevated temperatures used during mixing operations. In the case of asphalts containing appreciable amounts of volatile materials, the drop in penetration may be caused by loss of these materials through evaporation. In the case of most asphalts, however, it has been shown that the hardening is caused by oxidation of certain constituents of the asphalt.

There are many factors which influence the occurrence and rate of failure of a bituminous pavement by gradual oxidation or weathering; among these being the susceptibility of the asphalt to oxidation, the average temperature to which the pavement is exposed, the density of the pavement, and the amount of asphaltic binder present in the mix. Since the oxidation of asphaltic materials is catalyzed by heat and by actinic light rays, oxidation begins on the surface of the pavement and progresses gradually downward. The surface becomes brittle, cracks appear which permit the entrance of air and moisture, and eventually the pavement fails.

Because of the high temperature (300 to 350 F.) used in mixing sheet asphalt or bituminous concrete made with asphalt cement, oxidation can occur very rapidly and there may be a significant drop in penetration before the mix is even in place. In this case, the expected life span of the pavement is materially shortened.

It is the purpose of this report to describe some of the physical effects of direct chlorination on road building asphalts, and to present experimental data suggesting that the loss of penetration resulting from oxidation may be materially reduced by treatment with chlorine.

## THEORETICAL BACKGROUND

Asphalt, either natural or manufactured, is a mixture of various organic compounds which have been arbitrarily classified as: (1) carboids, that fraction of the asphalt which

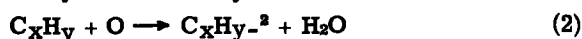
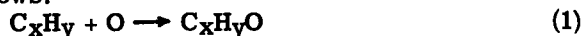
is insoluble in carbon disulfide; (2) carbenes, the fraction which is insoluble in carbon tetrachloride but soluble in carbon disulfide; (3) asphaltenes, which are soluble in carbon tetrachloride but insoluble in low boiling saturated hydrocarbons; and (4) maltenes, which are soluble in low boiling saturated hydrocarbons such as pentant (12). These constituents exist in asphalt in varying proportions as a colloidal mixture, the asphaltenes making up the major portion of the disperse phase, while the intermicellular phase consists primarily of the maltenes. Except in highly cracked or oxidized asphalts, the percentage of carbenes and carboids is very low.

About 35 to 60 percent of the compounds in the maltene group are saturated paraffinic compounds. From 10 to 30 percent are alicyclic compounds of the cyclohexane type, and the balance of the maltene fraction is made up of aromatic compounds either in aromatic structure or in various combinations with the paraffins and alicyclic compounds.

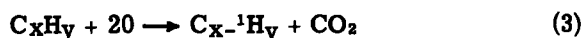
Little is known concerning the true nature of the asphaltenes. Analysis has shown, however, that they can be considered as "consisting of aromatic hydrocarbons containing paraffin chains to a varying extent, depending on the origin and manufacture of the bitumen" (12).

Oxidation of an asphalt at either high or low temperature results in a brittle, gel-type colloid if the oxidation is carried far enough. According to Abraham:

The effect of oxidation is two-fold, and involves the direct union of oxygen with the bituminous substances, also the elimination of a portion of the hydrogen or carbon in the form of water or  $\text{CO}_2$ . These reactions may be expressed roughly as follows:



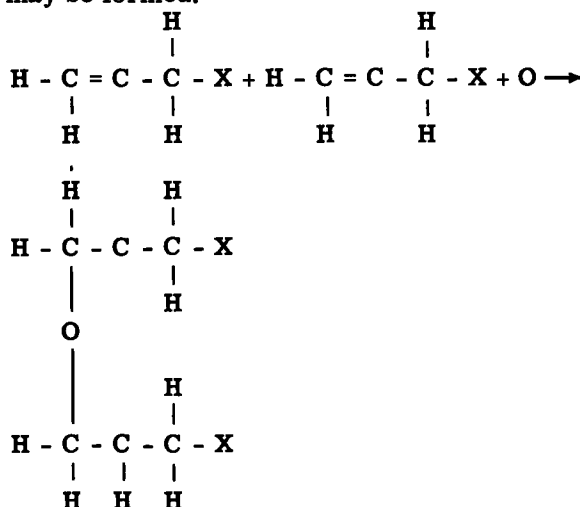
also



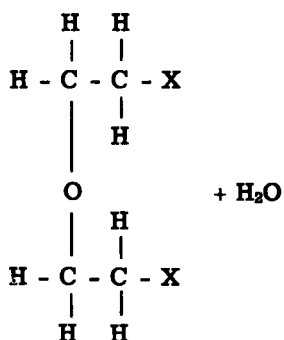
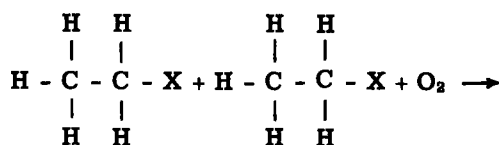
(1, p. 1464)

A reaction of Type 2 requires a greater amount of activating energy such as heat or actinic light rays than a reaction such as that indicated by Equation 1, while a reaction of the type shown in Equation 3 requires still further amounts of energy to progress in the direction indicated. It is highly improbable that oxidation of Type 3 could occur even at the elevated temperatures used at the mixing plant.

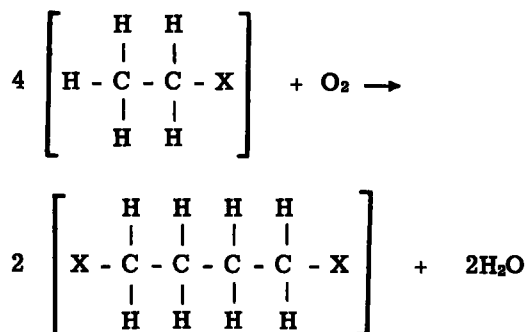
From the standpoint of molecular structure, oxidation without doubt results in the formation of larger molecules through reactions closely akin to polymerization and co-condensation. In the case of oxidation by simple addition, cross-linkages of an "ether bridge" type may be formed:



In the case of oxidation of the second type, cross-linkages may be formed with the elimination of hydrogen as water:



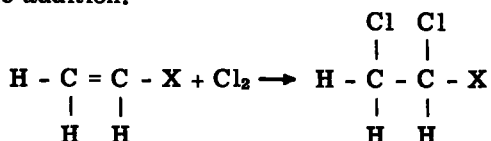
Or a sort of polymerization may take place with elimination of hydrogen and no addition of oxygen:



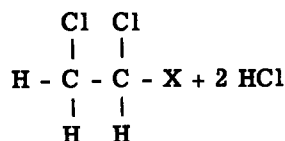
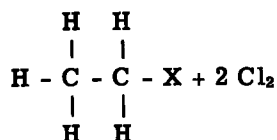
In any case, these reactions tend to result in a gel structure of the formation of cross-linked "chain" type molecules. This results at first in an increase in elastic properties of the asphalt, and finally in brittleness as the reaction proceeds further and further.

Although Pfeiffer speaks repeatedly of asphaltene formation as a result of oxidation, there is no indication that compounds are formed which resemble the asphaltenes chemically. During oxidation, as has been shown above, compounds are formed which have larger molecules and a more complex molecular structure. These compounds are less soluble than the original compounds in low boiling hydrocarbons such as pentane, they have higher melting points, and in most cases they would tend to be more brittle and less ductile. It is therefore to be expected that an oxidized asphalt would have a lower penetration, a higher R and B temperature and that it would be less ductile than the original material.

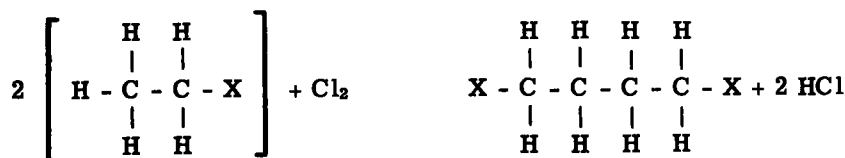
The action of chlorine on asphalt is in many respects similar to the action of oxygen. If any compounds are present in the asphalt with olefinic double bonds, the reaction will be one of simple addition:



No cross-linkages will be formed, since chlorine is monovalent. Chlorine may also react with the hydrocarbons with the elimination of hydrogen in the form of hydrochloric acid:



or



As in the case of oxidation, the simple addition reaction will take place more rapidly at lower temperatures than the reactions involving the elimination of hydrogen.

The idea of chlorinating asphalt is not new, and some of the properties of asphalt treated with comparatively large amounts of chlorine have been investigated.

Reaction with chlorine is an alternative technique by which asphaltic bitumen possessing certain special properties can be produced.

The action of chlorine is like that of sulfur and oxygen, i. e. chlorine withdraws hydrogen. The greater part of the added chlorine escapes in the form of hydrochloric acid.

Just as with sulfur, this reaction takes place at a lower temperature than is the case with oxygen, proceeding with ease at 200 C. . . . the action of the chlorine (compared with that of oxygen) on a Venezuelan asphaltic bitumen is shown in the following table.

The considerable analogy between the action of chlorine and that of oxygen is evident. A little more chlorine is, however, combined in the bitumen (12, p. 146).

TABLE 1

Treatment of Venezuelan Bitumen with Chlorine

(base stock: pen. at 25 C. 178, temp. R&B 39.5 C.) 60/80 asphaltenes 12.3%

Experimental Conditions	Treatment with Chlorine	Blowing with air
Temperature, deg. Centigrade	200	250
Consumption of agent per kilogram of asphalt	78g. Cl <sub>2</sub>	21g. O <sub>2</sub>
Volatile reaction products formed	73g. HCl	abt. 22.5g. H <sub>2</sub> O
Hydrogen withdrawn from asphalt	2g.	2.5g
Agent absorbed (calculated)	7g. Cl <sub>2</sub>	abt. 1 g. O <sub>2</sub>
Properties of final products:		
Pen. at 25 C.	26	22
Temp. R&B	82	84
60/80 asphaltenes, %	26.3	28.4

(12. p. 147)

It can be seen from this table that both chlorination and oxidation of asphalt result in a decrease in penetration, an increase in R & B temperature, and an increase in the "asphaltene" content (percentage of the asphalt insoluble in a mixture of paraffinic hydrocarbons with a boiling range between 60-80 C.).

The change in physical properties which occur as a result of causing 78 grams of chlorine to react with 1 kg. of asphalt are practically identical with the changes which occur as a result of the action of 21 grams of oxygen on the same asphalt. If, molecule for molecule, the action of chlorine were identical with that of oxygen, it would be reasonable to expect that much less than 78 grams of chlorine would be required to produce this result. However, as has been explained previously, the "ether bridge," or cross-

linking type of reaction does not occur with chlorination. Therefore it is to be expected that the average molecular weight of the compounds formed by chlorination will be lower than that of the compounds formed by oxidation. If a sample of asphalt is treated with a given molecular quantity of oxygen, and another sample of equal weight is treated with the same molecular quantity of chlorine, the physical properties of the sample subjected to chlorination will change in the same direction as those of the oxidized sample, but to a much smaller extent.

When an asphalt is subjected to direct chlorination, the first reaction which takes place is one of simple addition at olefinic double bonds. These compounds will not be as easily oxidized as the unchlorinated compounds since they are now "saturated." As chlorination progresses, hydrogen will be displaced by chlorine at other reactive points in the molecules. Although some polymerization will take place, the loss in penetration and ductility of the asphalt will not be as great as if a comparable amount of oxidation had occurred. Furthermore, future oxidation will be retarded, since oxidation cannot take place at those points in the molecule which have already reacted with chlorine.

### LABORATORY PROCEDURES

Eight samples of paving asphalt obtained from various manufacturers were tested in the laboratory. Of these samples, four were subjected to chlorination to determine the change in physical properties, any increase or decrease in resistance to oxidation, etc. Data furnished by the manufacturers is as follows:

Asphalt A. 100/120 penetration paving asphalt.

Asphalt B. 20/30 penetration pressure still tar produced as a result of cracking operations. M. P. 120-130 F.

Asphalt C. Flash point (deg. Fahrenheit)-575; penetration, 77 F. -67; ductility, 77 F. -150; ductility, 60 F. -150; sp. gr., 77 F. -1.019; sol.  $\text{CCl}_4$ , % -99.7; oliensis spot test-negative.

After Shattuck oxidation test: penetration, 77 F. -25; ductility, 77 F. -150.

Asphalt D. Flash point (deg. Fahrenheit)-585; penetration, 77 F. -66; ductility, 77 F. -150; ductility, 60 F. -150; sp. gr., 77 F. -1.1016; sol.  $\text{CCl}_4$ , % -99.8; oliensis spot test-negative.

After Shattuck oxidation test: penetration, 77 F. -45; ductility, 77 F. -150.

Asphalt E. 85/100 penetration paving asphalt from West Texas crude.

Asphalt F. 85/100 penetration paving asphalt from Near East crude.

Asphalt G. 85/100 penetration paving asphalt from Kansas crude.

Asphalt H. 85/100 penetration paving asphalt from Wyoming crude.

Asphalts E, F, G, and H were products of the same company, and asphalts E and F were produced at the same refinery. According to the manufacturer, asphalt B "is a pressure still tar which by nature of having been produced as a result of cracking operations contains a high percentage of unsaturated hydrocarbons."

### Chlorination

Samples of each asphalt under consideration were treated with two different quantities of chlorine and tested to measure the change in physical properties, resistance to oxidation, etc.

Chlorination was carried out in the laboratory by "blowing" the asphalt with dry chlorine at a temperature of 150 C. This comparatively low temperature was chosen to favor simple addition reactions over those involving substitution. Chlorine was "blown" through 500-gram samples of asphalt with constant agitation at a rate of 100 cc. per minute. The reactions were carried out in 1 liter Erlenmeyer flasks.

In an attempt to determine the degree of chlorination which would produce the best overall results, each asphalt was chlorinated to the point where hydrogen chloride was evolved at the reaction temperature. The evolution of hydrogen chloride was detected by passing the gases emerging from the reaction flask first over dry mercury, and then into a beaker containing a solution of silver nitrate. Any chlorine present in the mixture of gases reacted with the mercury to form mercuric chloride. The presence of hydrogen chloride in the mixture was detected by a dense white precipitate of silver chloride

in the silver nitrate solution. After chlorination, the asphalt was heated to 200 C. for a period of 30 minutes to drive off any remaining hydrogen chloride.

The change in physical properties of the asphalt (i. e. loss in ductility and penetration) resulting from this first attempt at chlorination was so great as to offset any advantage gained in reducing the oxidizability. Therefore, a smaller amount of chlorine was used in treating the second series of samples.

Because of time limitations, tests were not run on chlorinated samples of asphalts E, F, G, and H. Except for a slightly higher penetration, the properties of E, F, G, and H resembled those of C and D.

### Tests on Physical Properties

Specifications for determining the R & B softening point, the ductility, and the penetration permit a cooling time in air of only  $\frac{1}{2}$  to 2 hours before immersion of the specimen in a water bath prior to the test. Pfeiffer has shown (12, pp. 157-160) that these properties may change considerably if the cooling time in air is increased or decreased only very slightly. Therefore specimens used in performing these tests were allowed to stand at room temperature for five days before immersion in the water bath. After a five-day "curing" period any change in properties which might result from allowing the specimens to remain in air at room temperature for an additional few hours would be negligible (12, p. 159).

Softening Point, Ring and Ball (AASHTO T 53-42). Except for the five-day curing period mentioned above, this test was performed exactly in accordance with the specifications. The results are summarized in Table 2.

Ductility (AASHTO T 51-44). Ductility tests were carried out at a temperature of 25 C. (77 F.). Except for the five-day curing period, the tests were carried out in accordance with specifications.

Penetration (AASHTO T 49-44). The penetration of each sample was obtained at 0 C. (32 F.) with a 200-gram weight, penetration time 60 seconds; at 25 C. (77 F.) with a 100-gram weight, penetration time 5 seconds; and where possible at 46.1 C. (115 F.) with a 50-gram weight and a penetration time of 5 seconds. Except for the five-day curing period, the tests were performed in accordance with the specifications.

Determination of the Percentage of Bitumen Soluble in Carbon Disulfide (AASHTO T 58-37). This test was performed in accordance with the specifications.

Percentage of Bitumen Insoluble in Paraffin Naphtha (AASHTO T 46-35). This test was performed in accordance with the specifications, except that pentane was used as the solvent rather than the higher boiling fraction specified.

### Tests of Susceptibility to Oxidation

All of the proposed tests for oxidizability of road asphalts suffer from one or both of two defects. Most of the tests are carried out at temperatures well above the maximum temperatures found in bituminous pavements in place. Under these circumstances, oxidation will be accelerated, which is desirable, but as explained in the preceding pages the percentage of substitution reactions (i. e. elimination of hydrogen as water) will be higher than it would be if the test were carried out at lower temperatures. These tests can be used to predict oxidation during mixing operations, but they may not correlate well with performance of an asphalt pavement subject to oxidation by weathering.

The second defect found in many of the tests is that at some point during the test the asphalt is extracted or dissolved in an organic solvent such as benzene or carbon tetrachloride. The solvent is distilled off, and standard tests are run on the residue. Although it is possible to prevent further oxidation during distillation by distilling under carbon dioxide, it is often not possible to get rid of all the solvent. Obviously a very small amount of solvent remaining in the residue will drastically alter the physical properties.

The well-known Shattuck test is a case in point. This test suffers from both the above-mentioned defects.

In 1942, A. P. Anderson, F. H. Stross, and A. Ellings of the Shell Development Company proposed two tests for predicting the susceptibility of an asphalt to oxidation. The

first of these tests is simple in nature and involves nothing more than measuring the loss of penetration on heating. The second test proposed by these authors involves oxidation of the asphalt in a bomb with gaseous oxygen under pressure. This test is particularly suitable for predicting oxidation under weathering conditions since the temperatures involved do not exceed 50 C.

According to the authors, a standard loss of penetration on heating test does not correlate very well with behavior of the asphalt in service because the original penetration of the asphalt is not taken into consideration. The loss of penetration on heating is expressed as a percentage of the original penetration.

A number of investigators have established the fact that when penetration of an asphalt drops below a certain point, the road in which the asphalt is incorporated will fail because of brittleness. The obvious conclusion, which also has been generally accepted in practice, is that a softer asphalt has the advantage over a harder asphalt of similar hardening characteristics, since the former will take longer to reach a critical penetration (5, p. 45).

The authors have developed the following method which takes into account the original penetration of the asphalt:

The asphalt specimen is heated, in the conventional manner, to 16 C. for 5 hours in a standard oven after which the penetration of the sample is taken; this process is then repeated. The logarithms of the penetrations after 5 and after 10 hours are plotted against time in hours. A straight line is drawn through the two points and extended to 10 penetration, which is used as the x axis. The intercept on the x axis gives some indication of the time required by the asphalt to drop to this penetration and is termed the resistance to hardening.

$$\text{Resistance to hardening} = 5 \left[ \frac{y_1 - 1}{y_1 - y_2} \right] + 5$$

$y_1$  log penetration after 5 hours' heating

$y_2$  log penetration after 10 hours' heating

(5, p. 46)

In order to correlate the results of this test and those of the oxygen bomb test with the performance of the asphalt in a pavement the authors use a service rating.

The service rating is a measure of the performance of an asphalt, and is derived from experimental paving sections in which the asphalts were used under mixing and laying conditions which were as well standardized as possible. These sections were strips of pavement laid in the San Francisco Bay Area which were uniformly subject to light traffic for the period of one year. The ratings were made visually according to the amount of raveling exhibited by the pavement and cannot lay claim to a precision greater than one unit. . . . Ratings 1 and 2 signify a very good performance, 4, 5, and 6 poor to very poor performance. The borderline cases are rated as 3 (5, p. 45).

In experiments conducted by Anderson, et al., the service rating showed only a fair correlation with results obtained in a standard loss of penetration on heating test. One asphalt which hardened as little as 12 percent had a service rating of 4, while another with a penetration drop of 20 percent performed excellently. The correlation of the service rating with the Resistance to Hardening value was, however, very high. All asphalts with a resistance to hardening value between 55 and 100 had service ratings of 3 or better, while asphalts with resistance to hardening values below 55 had poor service ratings.

In spite of the high correlation of the results of this test with in-service performance ratings of the asphalt, the test suffers from the disadvantage that the asphalt is heated to 160 C. In order to eliminate the effect of high temperatures, Anderson, Stross, and Ellings developed a test in which the oxidation takes place at 50 C.

. . . the time necessary for an asphalt to drop to the critical penetration under standardized oxidizing conditions should be a measure of the durability of an asphalt. Since the attainment of the penetration would in

most cases take too long at the low test temperatures stipulated, it is necessary to develop a method of predicting this time from the behavior at shorter times. Direct extrapolation proved impossible, for it was found experimentally that the penetration is not a simple function of time.

The solution found was to combine the oxygen-absorption behavior of the asphalt, in amount and rate at a fixed time, with the hardening caused by a given oxygen absorption.

The oxidation is carried out in a stainless-steel bomb. . . .

The bomb is immersed . . . in an oil bath which can be regulated to 0.1 C. at the working temperature. For observation of the pressure, an automatic recorder, or for more accurate work, a Bourdon-type gage which can be estimated to 0.2 psi. can be used.

One hundred grams of the warm asphalt are poured into a 240-ml. (8-ounce) oil-sample bottle containing 67 grams of C. P. benzene. After weighing, the bottle is shaken until the solution is homogeneous; when it has reached room temperature, it is placed in the bomb, which is at 25 C. Next, the bomb is sealed and flushed with oxygen by charging it to 100 p. s. i. g. . . . and releasing it again. The flushing is repeated and the bomb is then charged with oxygen at slightly more than 100 p. s. i. g. After a short period (15 minutes) to test for possible leaks, the pressure is adjusted to 100 p. s. i. g. and the temperature is raised to 50 C. The pressure is recorded from now on, either continuously by automatic recorder or manually, as required for the plot described below. For each asphalt a run of 40 hours (or longer, for greater accuracy) . . . and several shorter runs of varying length are made. At the end of each run, the oxygen is released, and the asphalt is recovered as soon as possible to prevent its hardening in the solution. . . . The penetration of the asphalt is then measured. The data so obtained are used in the following manner:

The pressure drop is found by subtracting the observed gage pressure from the pressure of the original system at 50 C. This datum pressure calculated from the gas law and corrected for the solubility of the oxygen in the solution, the increase in vapor pressure of the benzene . . . is approximately 108 p. s. i. g. for the system under consideration. This value . . . was used in all calculations.

The pressure drop is plotted against time. . . . From this graph, the pressure drop at 40 hours and the slope of the tangent at this point (in psi. per hour) are evaluated. The product of the pressure drop and the slope is called the oxidation rating. . . .

Next, the logarithm of the penetration after oxidation is plotted against the pressure drop. . . . The amount of oxygen needed to reduce the penetration to the value of 20 is obtained by extrapolation and is called the hardening rating and is expressed in psi.

The deterioration index indicative of the service behavior of an asphalt is obtained from the two quantities as follows:

$$\text{Deterioration index} = \frac{\text{oxidation rating}}{\text{hardening rating}} \times 100$$

The oxidation rating relates the oxygen consumption of the asphalt to time by multiplying the oxygen pressure drop at 40 hours by the rate of oxygen consumption at that time. . . .

The hardening rating was derived from the linear relationship which was found to exist between the oxygen consumption and the logarithm of penetration. . . .

The ratio of the two ratings gives the desired relation of critical oxygen consumption to time and . . . is expressed directly in psi. per hour; it therefore has the dimensions of a rate, and represents the rate at which asphalts deteriorate (5, p. 47-49).

In experiments carried out by the authors, this test correlated very well with the service ratings of the asphalt. A deterioration index lower than 15 indicates fully satis-



TABLE 2  
PHYSICAL PROPERTIES AND SUSCEPTIBILITY TO OXIDATION OF  
CHLORINATED AND UNCHLORINATED ASPHALTS

Asphalt	Percent increase in weight resulting from chlorination	Temp. R. & B., C.	Penetration, 0 C., 200 g., 60 sec.	Penetration, 25 C., 100 g., 10 sec.	Penetration, 25 C., 100 g., 10 sec.	Penetration, 46.1 C., 50 g., 5 sec.	Penetration, 25 C., 100 g., 5 sec. after 5 hours' heating	Penetration, 25 C., 100 g., 5 sec. after 10 hours' heating	Ductility, 25 C.	Ratio Pen. 46.1 C., 50 g., 5 sec. Pen. 25 C., 100 g., 5 sec.	Susceptibility Factor	Slope, log. time vs. log. penetration curve	Class (according to Pfeiffer)	Percent by weight soluble in carbon disulfide	Percent by weight insoluble in pentane	Loss of weight on heating 10 hours, percent	Loss of penetration on heating 10 hours, percent	Resistance to Hardening	Deterioration Index
A no Cl <sub>2</sub>	44	37	82	107	352	75	69	100+	4.3	3.8	0.38	II	100	21.5	0.01	15.8	123	2.3	
A 0.118	49	30	61	79	262	61	59	100+	4.3	3.8	0.37	II	100	23.3	0.01	3.1	269	1.9	
A 0.495	58	9	23	29	92	24	24	24.5	4.0	3.6	0.32	II	100	27.1	0.01	-4.4		1.9	
B no Cl <sub>2</sub>	48	8	21	29	99	17	13	100+	4.7	4.3	0.46	I	100	26.2	0.04	38.1	15	19.8	
B 0.383	55	2	15	19	66	15	15	100+	4.4	4.3	0.39	II	100	31.2	0.01	0		2.1	
B 0.735	64	3	10	12	39	11	10	10.5	3.9	3.6	0.25	II	99.7	37.7	0.01	0		2.4	
C no Cl <sub>2</sub>	47	21	42	55	185	33	26	100+	4.4	3.9	0.41	II	100	23.8	-0.03	38.1	30	15.4	
C 0.187	54	11	34	43	141	33	33	100+	4.3	3.8	0.38	II	100	26.1	0.01	2.9		5.3	
C 0.431	62	7	15	19	61	14	16	34.5	4.1	3.7	0.33	II	100	30.3	0.01	-6.7		2.0	
D no Cl <sub>2</sub>	46	18	47	61	201	40	34	100+	4.3	3.9	0.39	II	100	22.4	0.01	27.6	48	13.1	
D 0.236	51	22	45	58	189	43	40	100+	4.2	3.7	0.37	II	100	25.7	0.01	11.1	105	3.1	
D 0.379	60	6	12	15	49	13	13	45.5	4.1	3.6	0.34	II	100	27.8	0.01	-8.3		2.0	
E no Cl <sub>2</sub>	44	19	63	84	277	44	31	100+	4.4	4.1	0.41	II	-	-	0.94	50.9	26	-	
F no Cl <sub>2</sub>	43	28	72	95	316	59	48	100+	4.4	4.0	0.40	II	-	-	0.91	33.3	48	-	
G no Cl <sub>2</sub>	46	26	65	84	273	54	45	100+	4.2	3.8	0.37	II	-	-	0.00	30.8	52	-	
H no Cl <sub>2</sub>	46	18	58	75	244	41	30	100+	4.2	3.9	0.36	II	-	-	0.01	48.2	28	-	

factory performance. If the index is above 20, poor durability can be expected.

In the laboratory the resistance to hardening test was carried out in accordance with the procedure outlined by Anderson, Stross, and Ellings. In obtaining penetration data, the specimens were allowed to "cure" for five days as previously described. The results are given in Table 2 and Figure 1. Owing to lack of a stainless steel bomb, it was necessary to modify somewhat the procedure outlined for performing the oxygen bomb test. In place of the bomb described by Anderson et al., use was made of small compressed gas cylinders known as "lecture bottles." These cylinders which are ordinarily used to dispense compressed gases for laboratory demonstration have a capacity of about 250 ml. and are fitted with a removable valve to facilitate refilling. In performing the test, the cylinder valves were removed, and the asphalt solutions were poured into the cylinders. The valves were then replaced, and the cylinders flushed and filled with oxygen as described by Anderson. Bourdon-type gages with scales reading from 0 to 100 psi. were then attached to the valves. The cylinders were then immersed in a water bath at 50 C.

In all other respects, the test was performed in accordance with Anderson's procedure. The results are given in Table 2.

It should be emphasized that this test was performed with equipment differing from that used by Anderson, and that the

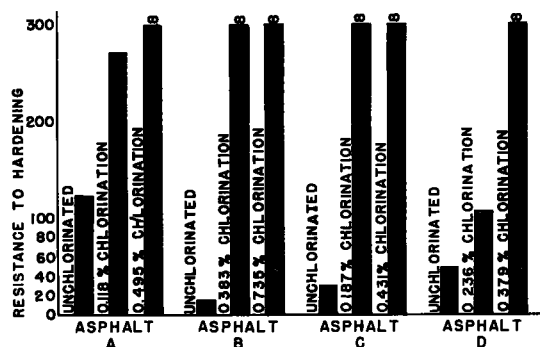


Figure 1. Resistance to hardening of chlorinated and unchlorinated asphalts.

values obtained from the deterioration index cannot be compared with those obtained by Anderson. Since it was impossible to standardize the equipment used with asphalts of known performance, the values obtained are purely relative.

### Stripping Test

A simple stripping test known as the Tyler wash test was performed with asphalts A, B, C, and D, both unchlorinated and chlorinated, to determine the comparative susceptibility to stripping action. Limestone and chert were used as aggregates.

For this test, described completely by Tyler (14), a 500-gram sample of each aggregate was coated with 5 percent by weight of each asphalt. After a 24-hour curing period, the coated aggregate was separated into particles and placed in a jar with one liter of distilled water. The jar was then placed in a rack built to fit into a standard Ro-tap machine and shaken for 30 minutes. The aggregate was removed from the jar, allowed to dry, and rated for stripping on a ten-point scale. On this scale, 0 denotes no stripping, 1 to 3 slight stripping, 4 to 7 moderate stripping, and 8 to 10 excessive stripping. Table 3 gives average values based on the ratings of four observers.

TABLE 3  
TYLER WASH TEST  
Degree of Stripping from Chert and Limestone using  
Unchlorinated and Chlorinated Asphalts

	Chert	Limestone
A - unchlorinated	3*	1
0.495% Cl <sub>2</sub>	1	1
B - unchlorinated	2	1
0.735% Cl <sub>2</sub>	1	1
C - unchlorinated	2	2
0.431% Cl <sub>2</sub>	0	1
D - unchlorinated	2	1
0.379% Cl <sub>2</sub>	1	1

\* 0 - 3, slight stripping; 4 - 6, moderate stripping;  
7 - 10, severe stripping.

### COMMENTS

The changes in physical properties resulting from chlorination of the asphalts tested are in complete agreement with theory. With increasing amounts of chlorination, the penetration at a given temperature is decreased, the ring and ball softening point is increased, the percentage by weight of the asphalt insoluble in pentane is increased, the slope of the log. time versus log. penetration curve is decreased, the temperature susceptibility factor is decreased, and the ductility is decreased. These changes all indicate that when an asphalt is chlorinated there is a tendency toward the formation of a gel structure.

The results obtained in the loss of penetration on heating test (resistance to hardening) suggest that it may be possible to reduce materially the loss of penetration due to high temperature oxidation by chlorinating the asphalt. No asphalts containing an appreciable amount of volatile material were used in the chlorination experiments. Therefore it can be assumed that any loss of penetration on heating was the result primarily of oxidation.

Since all penetration tests were performed after a five-day "curing" period, and since the values thus obtained are considerably lower than when the test is performed according to AASHTO standards, the resistance to hardening value of 55 used by Anderson to differentiate between asphalts which perform well and those which perform poorly does not apply. In the case of the results obtained in the laboratory, the critical value of resistance to hardening would be several points lower than 55.

The results obtained in the oxygen bomb test should not be considered conclusive.

The use of high temperatures during oxidation is avoided in this test, but the asphalt is dissolved in a solvent (benzene) from which it is later recovered. Although the benzene was distilled off under carbon dioxide, thus preventing further oxidation of the asphalt, it was impossible to be certain that all the benzene was eliminated. As explained previously, a very small amount of benzene remaining in the asphalt will cause a considerable increase in penetration.

According to results obtained in the Tyler wash test (Table 3), chlorination of an asphalt does not increase its tendency to strip from either a siliceous aggregate, such as chert, or a carbonate rock such as limestone. In fact, the data suggest that the opposite may be true; chlorination may increase the adhesiveness of the asphalt in the presence of water. If this is the case, it can be explained by the fact that chlorination increases the polarity of certain constituents of the asphalt.

### CONCLUSIONS

1. Treatment of the asphalt samples tested in the laboratory with only a very small amount of chlorine (0.1 - 0.35 percent increase in weight of the asphalt) results in a very great increase in the resistance to hardening of the asphalt. Further treatment with chlorine does not result in a significant increase in resistance to hardening but may lower the ductility of the asphalt to a point where it is no longer useful for highway construction.

2. Chlorination of an asphalt does not increase its tendency to strip from mineral aggregates in the presence of water.

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