

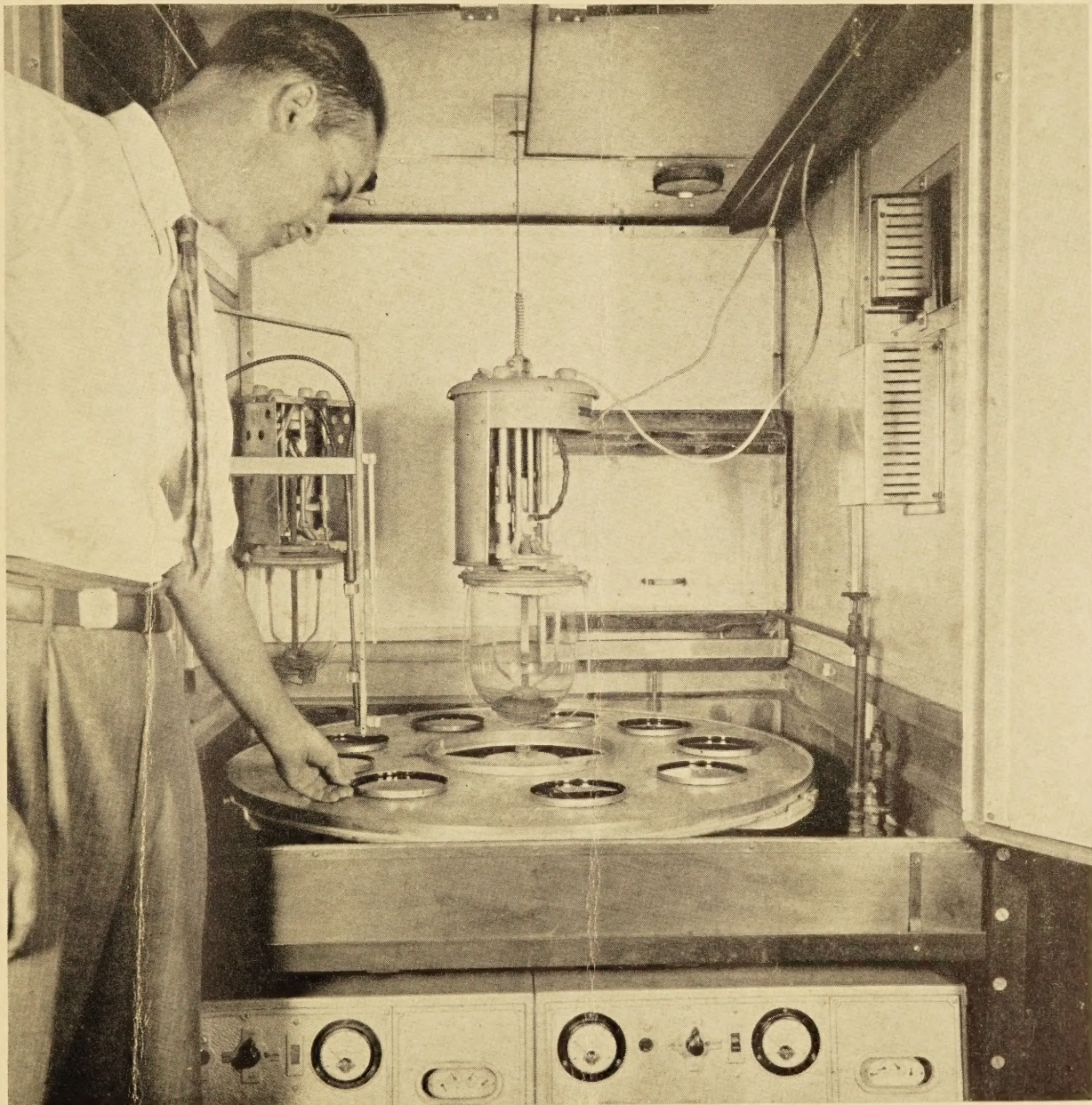
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SUBJECTING TAR SAMPLES TO ACCELERATED WEATHERING TEST

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W. S. Sullivan 3/18/43

THE SULFONATION INDEX TEST FOR ROAD TAR¹

BY THE DIVISION OF TESTS, PUBLIC ROADS ADMINISTRATION

Reported by R. H. LEWIS, Senior Chemist, and W. J. HALSTEAD, Associate Chemist

IN RECENT YEARS several States have reported unsatisfactory service behavior with certain road tars which in all respects met the requirements of the controlling specifications. Priming material did not set up in normal curing time, delaying construction of the finished surface. The residual tars became greasy, showed evidence of separation or nonhomogeneity, and did not adequately hold the cover stone, necessitating early replacement of the road surface.

A study of these unusual conditions in areas where tar products had given excellent service for many years indicated that high percentages of paraffinic hydrocarbons were present in some of the tars that had not proved satisfactory. It was believed that in most cases this condition resulted from the use of petroleum products as a flux in the manufacturing process. However, it has been indicated also that some road tars derived from water-gas tar contain sufficiently high amounts of paraffinic material to affect adversely the quality, binding characteristics, and weathering properties of the tars.

In order to improve the performance of these road tars, it was recommended that the percentage of distillate at the various cutting temperatures used in the distillation test be more closely specified and that a maximum requirement for a sulfonation index of the distillation fractions, 0° to 300° C. and 300° to 355° C., be included in the specifications for road tars of the cold application type. The requirements for grades RT-1 to RT-6, inclusive, as proposed by some of the tar producers to meet this situation, and the standard specifications of the American Association of State Highway Officials, are given in table 1.

The specifications suggested by the producers were in use in some localities during 1940. Some users added the proposed limits for sulfonation index to the existing A. A. S. H. O. specifications; others changed the requirements for the sulfonation index on the 300° to

The erratic behavior of some tar products in localities where tars have given excellent service for many years has led to specifications limiting the amount of paraffinic and naphthenic hydrocarbons that they may contain. The amount of these materials is controlled by maximum requirements for the sulfonation indexes of two fractions of the tar distillate. The sulfonation indexes are determined by treating portions of the 0-300° C. fraction and the 300-355° C. fraction of the distillate with 37 normal sulfuric acid under specified test conditions. The volume of the unsulfonated residue expressed in millimeters in each fraction per 100 grams of tar is reported as the sulfonation index for that fraction.

This report briefly discusses the types of hydrocarbons present in asphaltic and tar products. It suggests modification in the test method for determining the sulfonation index that will insure more reproducible and more accurate results. It demonstrates that the solubility of tar distillates in dimethyl sulfate and diethyl sulfate can not be used as a quantitative test for the paraffinic and naphthenic hydrocarbons.

A study of the relationship between the sulfonation indexes and the weathering properties of tars was made by exposing 1/8-inch films of the tar and compressed sand-tar mixtures to the accelerated weathering conditions of the weatherometer. These studies indicate that tars with the higher sulfonation indexes show the greater hardening which is caused by factors other than loss of volatile material, and also that those materials with a high sulfonation index on the 300°-355° C. fraction develop a lower bonding strength than those which have low sulfonation indexes for this fraction. However, the abnormal behavior of some of the tars during the laboratory tests and the wide differences in the characteristics of tars meeting the same specification indicate that a definite correlation of the sulfonation index with actual road behavior will be difficult to obtain.

355° C. fraction from not more than 1.0 to not more than 1.5. As is noted in table 1, the A. A. S. H. O. now includes an optional requirement for the sulfonation index in its Specification M 52-42. This requirement applies to the grades RT-1 through RT-6 and the limits for the 0° to 300° C. fraction are the same as those proposed by some producers (Specification A, table 1) while the limit for the 300° to 355° C. fraction has been increased to not more than 1.5.

Although the sulfonation test has been used in the analysis of tar distillates for many years, it has not been employed extensively in the routine examination of road tars. This study of the sulfonation index test and the effect of the unsulfonated portion of the tar on its behavior under laboratory accelerated weathering conditions may, therefore, prove of interest to the users of road tars.

FOUR CLASSES OF HYDROCARBONS PRESENT IN BITUMINOUS MATERIALS

The significance and limitations of the sulfonation index test cannot be readily understood without some knowledge of the types of hydrocarbons that are constituents of both petroleum and tar products and which vary in quantity, depending on the source of the base material and the process used in refining. There are generally four large classes or divisions of hydrocarbons commonly present in petroleum and tars of all types. They are: (1) The paraffinic, which are the saturated, straight chain group; (2) the naphthenic, which are cyclic saturated compounds; (3) the olefinic, which are the unsaturated, straight-chain group; and (4) the aromatics, which are the derivatives and homologues of benzene.

Crude petroleum contains all of these groups in various proportions but generally the greatest percentage of hydrocarbons present is paraffinic or naphthenic. Products from the cracking of petroleum or petroleum distillates contain high percentages of the unsaturated or olefinic group and the aromatics.

¹ Also known as the sulfonation factor.

TABLE 1.—Comparison of road tar specifications¹

	Grade RT-1		Grade RT-2		Grade RT-3		Grade RT-4		Grade RT-5		Grade RT-6	
	Specifica- tion A	Specifica- tion B	Specifica- tion A	Specifica- tion B	Specifica- tion A	Specifica- tion B	Specifica- tion A	Specifica- tion B	Specifica- tion A	Specifica- tion B	Specifica- tion A	Specifica- tion B
Engler specific viscosity, at 40° C	5-8	5-8	8-13	8-13	13-22	13-22	22-35	22-35				
Engler specific viscosity, at 50° C									17-26	17-26	26-40	26-40
Specific gravity at 25°/25° C	1.09+	1.08+	1.10+	1.08+	1.10+	1.09+	1.11+	1.09+	1.12+	1.10+	1.13+	1.10+
Total bitumen, soluble in CS ₂ . . . percent	88+	88+	88+	88+	88+	88+	88+	88+	83+	83+	83+	83+
Water, percent by weight	2-	2-	2-	2-	2-	2-	2-	2-	1.5-	1.5-	1.5-	1.5-
Distillation, per cent by weight:												
0°-170°	3-	7-	3-	7-	2-	7-	2-	5-	2-	5-	2-	5-
0°-200°	6-		6-		5-		5-		5-		5-	
0°-235°	6-22		5-18		4-16		3-15		2-13		2-12	
0°-270°	16-32	35-	14-28	35-	11-27	30-	9-25	30-	8-22	25-	6-20	25-
0°-300°	24-40	45-	21-37	45-	17-34	40-	16-32	40-	15-31	35-	14-30	35-
Softening point (R&B) distillation residue	30-60	30-60	35-60	30-60	35-60	35-65	35-60	35-65	35-65	35-70	35-65	35-70
Sulfonation index: ²												
Total distillate to 300° C	8-		7-		6-		6-		5-		5-	
Distillate between 300° and 355° C	1-		1-		1-		1-		1-		1-	

¹ Specification A proposed by some producers; specification B, A. A. S. H. O. Specification M52-42.

² The A. A. S. H. O. provides optional requirements for the sulfonation index, the limits being the same as those recorded under specification A for the 0°-300° C. fraction. The requirement for the 300°-355° C. fraction is 1.5- for all grades.

The composition of coal tar varies widely, depending on the source of the coal, the method of manufacture, and the temperature conditions at the time of manufacture. Crude tars of all types contain tar acids and bases in various percentages but, since these are generally removed by refining before the material is marketed as a road tar, the hydrocarbons of the neutral oil fraction are of primary concern.

High-temperature tars are manufactured at temperatures of approximately 1,200° C. They contain chiefly aromatic hydrocarbons in the neutral oil fraction. When they are distilled from vertical retorts, they contain considerable amounts of paraffinic and unsaturated substances not found in coke-oven or horizontal-retort tars. The percentages of these classes of hydrocarbons in vertical-retort tar, however, are not as large as in the case of low-temperature tar.² Low-temperature tars are manufactured at carbonization temperatures around 600° C. They contain about 20 to 40 percent aromatics, 18 to 40 percent unsaturated, and 34 to 43 percent saturated hydrocarbons.³ They are not generally manufactured in this country and are not encountered in road-tar manufacture. A small amount of vertical retort tar is used, but the major proportion of coal tars used as the raw products for manufacturing road tars are those obtained from other gas works and coke ovens, equipped to recover byproducts, with the latter representing about 78 percent of the total.⁴

In addition to the coal tars, large quantities of water-gas tars are also used in manufacturing road materials. These tars are the byproducts of the commercial processes for manufacturing water gas and are derived from the gas oil or fuel oil used in carbureting or enriching the water gas. Water-gas tars vary widely in composition and may be chiefly aromatic or may contain high percentages of paraffinic or naphthenic materials, depending on the carbureting oil and the manufacturing conditions.

TARS DIFFER WIDELY IN PHYSICAL AND CHEMICAL PROPERTIES

W. W. Odell,⁵ in discussing the chemical properties of water-gas tar, makes the following statement:

* * * it may be composed entirely of substances formed by the cracking of the oil or it may contain an appreciable amount

² High Temperature Coal Tars, by W. G. Adams. Science of Petroleum, vol. IV, pp. 3118-3127.

³ Low-Temperature Tar Oils, by J. G. King. Science of Petroleum, vol. IV, pp. 3113-3117.

⁴ Asphalt and Allied Substances, 4th ed., Abraham, p. 344.

⁵ Technical Paper No. 304, Bureau of Mines, United States Department of the Interior.

of the original constituents of the oil. It is not uniform in character and quality, rather the product of one plant is frequently altogether different from that of another plant. The reasons for these differences are that the operating conditions, oil used, gas standard, etc., are not the same in all plants.

In the same paper Odell gives the approximate limits between which various properties of the tar may lie. These are:

Specific gravity—from 1.00 to 1.18.

Fluidity—from thin fluid-like oil to viscous, heavy liquid.

Free carbon—from 1.0 percent or less to 6.0 percent or more.

Solids in distillate fractions—from 0 to more than 10 percent.

Distillation residue at 355° C. (vapor temp.)—from 40 to 70 percent.

Sulfonation residue—from 5 to 25 percent.

The same author also points out the effect of several factors involved as follows:

Temperature:

It is usually conceded that if the temperature is too low, appreciably lower than 1,300° F., the oil will not be completely cracked * * *. Likewise, it is generally known that excessively high temperatures are favorable to the formation of naphthalene and carbon.

Rate of oil input:

* * * with a slow rate of input, the oil, if effectively sprayed, will be more completely cracked and a higher gravity tar produced than when the oil is injected more rapidly.

Distribution of oil:

That proper spraying of the oil, its distribution over the surface of the carburetor brickwork, is essential for efficient cracking is well known * * *.

Kind of oil used:

* * * the writer is led to believe that when some of the heavy viscous oils are used, a higher temperature is required in the checker chambers to crack them properly * * *.

Condition of checker brick:

The tar formed when the brickwork is "dirty" contains more uncracked oils—saturated hydrocarbons—less "solids" in the distillation fractions and has a lower specific gravity * * *.

From this brief discussion it is seen that many types of crude tars are available to the road tar refiner and that these tars may differ widely in their physical and chemical properties. The standard specifications, RT 143 and M 52-42, for tars for use in road construction, issued by the Federal Specifications Executive Committee and the American Association of State Highway Officials, respectively, contain a general requirement that reads as follows: "Materials furnished under this specification shall be prepared from suitable gas-house,

coke-oven, and/or water-gas tars." Road tars may be, therefore, a product from one source or they may be blends of several types from one or many sources; so that the problem of explaining the service behavior on the basis of the quantity and types of various hydrocarbons present becomes very complex and is one that will require considerable study.

The reactivity of each of the groups of hydrocarbons with sulfuric acid varies widely and this fact is used as the basis for the sulfonation test. The paraffinic hydrocarbons are not attacked appreciably by H_2SO_4 except for a very slow reaction when 12 to 15 percent fuming sulfuric acid is used; the naphthenic hydrocarbons exhibit essentially the same behavior but are a little less resistant. The olefinic or unsaturated group will react readily with 75 percent acid; and the aromatic compounds require acid of about 95.6 percent strength for complete reaction. The sulfonation test provides for the use of an excess of 98.61 percent acid at $100^\circ C.$ for 1 hour. Thus, it is considered that all the aromatic and unsaturated hydrocarbons are oxidized or converted into sulfonic acids while the paraffins and naphthenes are essentially unaffected.

It should be noted that while paraffinic and naphthenic hydrocarbons are the classes usually found in uncracked petroleum, and the coal tars most generally used for road purposes in this country contain very little of these groups, the sulfonation test is not a direct test for petroleum products, but a test for certain groups of hydrocarbons. These hydrocarbons may originate in either petroleum or coal tar and their absence or presence in a road material is not a definite indication of the parent substance of that material.

VARIATIONS IN TEST PROCEDURE INFLUENCED RESULTS OF SULFONATION INDEX TEST

As shown in table 1, the sulfonation test is made on two portions of the tar distillate; one, the fraction distilling off up to $300^\circ C.$, and the other, the fraction distilling off between 300° to $355^\circ C.$ The method proposed by the producers for making the test follows essentially the same procedure as that used in the Barrett Company's Method H-15.⁶ However, the results are expressed as a sulfonation factor (or index), which is the volume of unsulfonated residue per 100 grams of tar. The method suggested is as follows:

SULFONATION INDEX TEST FOR ROAD TAR

Apparatus.

Babcock test bottles. The graduated portion of the stem shall have a capacity of 2.0 milliliters divided into 10 major divisions. Each major division to have 5 or 10 subdivisions.

Centrifuge, for Babcock test bottles.

Method.

Ten grams (10.0 ± 0.1 gram) of the distillate or fraction of distillate to be tested shall be weighed into a Babcock test bottle. To this shall be added 30 milliliters of 37 times normal sulfuric acid (80.07 percent total SO_3), 10 milliliters at a time. The bottle with its contents shall be shaken for 2 minutes after each addition of 10 milliliters of acid. A thorough mixing of sample and acid is essential. After 30 milliliters of acid has been added the bottle shall be kept at a constant temperature of from $98^\circ C.$ to $100^\circ C.$ for 1 hour, during which time it shall be shaken vigorously every 10 minutes. At the end of an hour the bottle shall be removed from the hot bath, cooled,

filled to the top of the graduated stem with ordinary sulfuric acid, and then whirled for 5 minutes in the centrifuge. The volume of unsulfonated residue shall then be read off from the graduations. The graduated portion of the bottle measures 2.0 milliliters and is divided into 10 major divisions, further graduated in 5 or 10 smaller divisions. The reading, in terms of the major divisions (0.2 milliliters) multiplied by 2, gives the results in terms of milliliters of sulfonation residue per 100 grams of distillate.

The sulfonation factor is the milliliters of sulfonation residue from 100 grams of the distillate multiplied by percentage of the distillate based on weight of the tar, divided by 100.

Notes.

The purpose of the test is to determine the amount of paraffins present. These must be distinguished from resins or other materials. (The paraffins are unchanged by the acid, but the resins may be produced by the interaction of certain oils with the acid.) Generally, the sulfonation residue is a clear, transparent oil. Occasionally, some white or even dark colored solid paraffin may be present. Also, from some oils, a solid resin may be formed. The latter is usually dark in color and does not melt at $100^\circ C.$ The paraffin will be liquid at that temperature. In case solid material (apparently paraffin) appears, which cannot be melted in the water bath without causing overflow from the bottle, a new test should be made. This is to be done in the same manner as previously except that when the bottle is removed from the hot bath it is not to be cooled before the addition of acid. Also, the addition of acid should be to a point below the top of the graduations to allow room for expansion. The bottle may then be whirled in the centrifuge for 3 minutes and again placed in the water bath. Again it may be centrifuged for 2 minutes. If material which appears as liquid in the bath solidifies during centrifuging, the final reading should be taken with the bottle still in or slightly raised from the bath.

If a separate layer of sulfonation residue cannot readily be observed, one or more drops of water shall be carefully added to the bottle. This sometimes calls attention to paraffin which, because of its color, might escape notice. It also sometimes aids in the measurement.

The addition of the acid should be regulated so that the mixture ceases to heat up on shaking, before another portion is added. If acid is added too quickly, foaming results.

Sometimes the contents of the bottle will start to foam on removal from the hot bath. Immersion in cold water will usually stop the foaming.

Proper strength of sulfuric acid is essential.

The 37N acid should contain 80.07 percent by weight of total SO_3 . It is prepared by mixing analyzed ordinary concentrated sulfuric acid with analyzed fuming sulfuric acid in proper proportions. (It is advisable to make a check test on the mixture to insure that the strength is correct).

Example.

95 percent sulfuric acid contains 77.5 percent by weight SO_3 .
98 percent sulfuric acid contains 80.0 percent by weight SO_3 .
15 percent fuming sulfuric acid contains 84.4 percent by weight SO_3 .

To prepare 37N acid (80.07 percent SO_3), 62 percent by weight (63 percent by volume) of 95 percent H_2SO_4 is mixed with 38 percent by weight (37 percent by volume) of 15 percent fuming H_2SO_4 .

If the volume of unsulfonated residue exceeds the capacity of the graduated stem (2.0 milliliters), the test may be made with 5 grams (5.0 ± 0.1 gram) of the distillate to be tested, adjusting the computation of results accordingly.

In this investigation the method as outlined was followed except that the samples were placed in the bath after the addition of 20 milliliters of acid and heated for 30 minutes with the required shaking at 10-minute intervals. After this time the final 10 milliliters of acid was added and the heating continued for the additional 30 minutes.

This modification of the procedure gave more favorable conditions for the escape of gases formed during the reaction and thus eliminated much of the difficulty

⁶ Methods of Testing Tar Products, Revised July 1931. The Barrett Company.

caused by foaming during the shaking. It also was necessary to use less than 10 grams of distillate in some cases where the volume of unsulfonated residue was large and exceeded 2 milliliters for the standard weight of sample. The use of a smaller sample for the 300° to 355° C. distillate was also found to be most convenient for certain materials as it eliminated the necessity of making two distillations to this higher temperature in order to obtain 10 grams of distillate.

Subsequent to the completion of tests to be reported later (table 6), it was found that the producers' method failed to give reproducible results in some cases, especially when the amount of unsulfonated residue was large. Accordingly, a brief study was made of the effect of variations in the test procedure on the value of the sulfonation index.

THREE TARS HAVING HIGH, MEDIUM, AND LOW SULFONATION INDEXES STUDIED

Three tars were used for this study: A, having high sulfonation indexes; B, having medium indexes; and C, having very little unsulfonated residue. Sufficient distillate for each tar was collected and combined so that all the tests for each distillate were made on portions of the same material. The properties of the distillates are given in table 2. The method as shown above was used with variations in the procedure as listed in table 3.

TABLE 2.—Properties of distillates used for studying the effect of various procedures on the results of sulfonation index test

Sample identification	Distillate up to 300° C.			Distillate between 300° and 355° C.		
	Percentage of sample	Specific gravity at 25° C.	Index of refraction at 38° C.	Percentage of sample	Specific gravity at 25° C.	Index of refraction at 38° C.
A	33.3	0.949	1.543	15.2	1.024	1.597
B	31.5	.973	1.562	13.9	1.055	1.619
C	34.6	1.023	1.589	11.3	1.113	(¹)

¹ Test not made; sample solid at 38° C.

TABLE 3.—Variations in test procedure for determining sulfonation index

	Procedure		
	No. 1	No. 2	No. 3
Amount of 37N acid in each portion..... milliliters	10	10	10
Number of portions added immediately.....	3	2	2
Total number of portions added.....	3	3	2
Time of heating before final addition of acid..... minutes	0	30	0
Total time of heating..... do	60	60	60
Time of shaking after initial portion of acid..... do	2	2	2
Time of shaking after each other portion of acid..... seconds	30	30	30
Time of shaking after each 10 minutes heating..... do	30	30	30

Procedure No. 1, with only a slight change in the amount of shaking, is the same as in the producers' method; procedure No. 2 is that used for the tests reported later (table 6); and procedure No. 3 is a further modification that reduces the danger of the sample foaming over. In addition to these modifications in technique, the weights of samples were also varied. The results of these tests are shown in tables 4 and 5. Table 4 shows the results for the distillates up to 300° C. and table 5 shows the results for the 300° to 355° C. fraction.

For sample A, the results for the distillate up to 300° C. show wide variations for the different pro-

cedures, values for the sulfonation index ranging from a minimum of 6.3 to a maximum of 8.5. The values of the sulfonation index of this sample show that, in general, procedure No. 1 gives slightly higher values than does procedure No. 2 for the same weight of sample.

TABLE 4.—Effect of various procedures on the results of the sulfonation index test for tar distillation up to 300° C.

DISTILLATE FROM SAMPLE A

Test No.	Approximate weight of sample	Procedure No.	Volume unsulfonated	Sulfonation index
	<i>Grams</i>		<i>Percent</i>	
1	10.0	1	23.1	8.1
2	7.5	1	22.8	8.0
3	5.0	1	20.7	7.3
4	10.0	2	22.5	7.9
5	7.5	2	21.3	7.5
6	5.0	2	19.5	6.8
7	10.0	3	21.7	7.6
8	5.0	3	18.8	6.6
9	5.0	3	19.6	6.9
10	5.0	3	19.0	6.6
11	5.0	3	18.4	6.5
12	5.0	(¹)	18.0	6.3
13	5.0	(²)	20.5	7.2
14	5.0	(³)	24.1	8.5

DISTILLATE FROM SAMPLE B

15	10.0	1	10.4	3.4
16	10.0	2	9.9	3.2
17	7.5	2	8.4	2.7
18	5.0	2	7.0	2.3
19	5.0	3	6.7	2.2
20	5.0	3	7.2	2.3
21	5.0	3	6.8	2.2
22	5.0	(¹)	6.8	2.2
23	5.0	(⁴)	10.4	3.4

DISTILLATE FROM SAMPLE C

24	10.0	2	1.2	0.4
25	7.5	2	1.0	.3
26	5.0	2	.8	.3
27	5.0	3	.8	.3

¹ Procedure 3 but with shaking at 5-minute intervals.
² Procedure 3 but with shaking at 15-minute intervals.
³ Procedure 3 but with 10 seconds shaking at 10-minute intervals.
⁴ Only 10 milliliters of 37N H₂SO₄ used.

TABLE 5.—Effect of various procedures on the results of the sulfonation index test for the distillates between 300 and 355° C.

DISTILLATE FROM SAMPLE A

Test No.	Approximate weight of sample	Procedure No.	Volume unsulfonated	Sulfonation index
	<i>Grams</i>		<i>Percent</i>	
1	10.0	1	15.4	2.3
2	7.5	1	13.8	2.1
3	5.0	1	13.0	1.9
4	10.0	2	16.4	2.4
5	7.5	2	15.4	2.3
6	5.0	2	13.9	2.1

DISTILLATE FROM SAMPLE B

7	7.5	2	7.7	1.0
8	5.0	2	7.4	1.0
9	5.0	3	6.5	.9
10	5.0	3	6.9	.9
11	5.0	3	7.0	.9

DISTILLATE FROM SAMPLE C

12	10.0	2	(¹)	(¹)
13	7.5	2	(¹)	(¹)
14	5.0	2	(¹)	(¹)
15	5.0	3	(¹)	(¹)

¹ Trace.

The results also vary in order of the weight of sample of distillate, the 10-gram sample giving the highest result and the 5-gram sample giving the lowest.

For tests made by procedure No. 3, test No. 7 using 10 grams of distillate gives a considerably higher result than do any of the tests with this procedure in which 5 grams of distillate were used (tests Nos. 8-11). This indicates that 20 milliliters of 37N acid are insufficient for complete reaction of the 10-gram sample. Consequently, procedure No. 3 was used only with a 5-gram sample in all other determinations.

Procedure No. 3 with a 5-gram sample generally gives lower results than either of the other methods and the results check well. Tests Nos. 12, 13, and 14 illustrate the importance of shaking. In test No. 12 the sample was shaken at 5-minute intervals and gave a value of 6.3 for the sulfonation index. In test No. 13 the sample was shaken at 15-minute intervals and gave a value of 7.2. In test No. 14 the sample was shaken 10 seconds after each addition of the acid instead of 2 minutes after the first addition and 30 seconds after the second, and during the heating period it was shaken at 10-minute intervals for 10 seconds. The value obtained for the sulfonation index was 8.5. These values indicate that thorough shaking is necessary for complete sulfonation.

The results on the distillate up to 300° C. for sample B also show the same general variations as those for sample A. Procedure No. 1 and procedure No. 2, using larger samples, give higher results than those for the 5-gram sample for procedure No. 2 and procedure No. 3. Test No. 23 was made using only 10 milliliters of 37N H₂SO₄ on a 5-gram sample and the result was high.

The tests on distillate up to 300° C. for sample C show the same order of results, but the amount of unsulfonated residue is so small that the experimental error in reading the volume is practically equal to the differences obtained.

The results on the distillates between 300° and 355° C. show less variation for the different methods than do those for the distillates up to 300° C., indicating that the reactions take place more easily for this fraction and that the variations in test procedure are of less importance.

Since it is known that some of the aromatic compounds (benzene and its homologues) are difficult to sulfonate and since the strength of the acid used in the test is insufficient to produce an appreciable reaction with the paraffinic and naphthenic hydrocarbons, it is most likely that the test procedure which gives the smallest amount of unsulfonated residue is the most accurate. Therefore, it is indicated from these tests that procedure No. 3 will give more accurate results than either of the other two methods.

MODIFIED METHOD OF TEST PROPOSED

In view of these results, it is recommended that the method of test be modified to provide for a 5-gram sample of distillate and for manipulation as outlined in procedure No. 3. It is believed that these modifications will insure more complete sulfonation of the aromatic hydrocarbons and give better reproducibility than do the former practices. The proposed method is as follows:

PROPOSED METHOD OF TEST FOR SULFONATION INDEX OF ROAD TAR

A. SCOPE

1. This method of test is intended for use in determining the sulfonation index of the total distillate to 300° C. or of the fraction of the distillate from 300° C. to 355° C., obtained by means of the A. A. S. H. O. Standard Method of Test for Distillation of Tars and Tar Products, T 52-35.

B. SOLUTIONS REQUIRED

2. (a) *Sulfuric acid (37N)*.—Prepare 37N H₂SO₄ by blending reagent-grade fuming and concentrated sulfuric acid to 98.61 ± 0.2 percent H₂SO₄, as determined by titration.

(b) *Sulfuric acid (specific gravity 1.84)*.

C. APPARATUS

3. The following apparatus is required:

(a) *Test bottles*.—The test bottles shall be made of good quality glass and shall be 6-inch, 18 grams, either 8 percent or 10 percent Babcock milk test bottles. The capacity to the base of the neck shall be 45 to 50 milliliters. The graduated portion of the bottle shall contain 1.60 ± 0.025 milliliters for the 8 percent test bottle and 2.00 ± 0.025 milliliters for the 10 percent test bottle (at a temperature of 77° F. (25° C.)). The 8 percent test bottle shall be graduated in 8 major divisions, each major division being further divided in 10 subdivisions, and the 10 percent test bottle shall be graduated in 10 major divisions, each major division being further divided into 5 or 10 subdivisions. Each line for the major divisions shall extend at least three-fourths of the distance around the neck and be numbered from the bottom 1, 2, 3, etc. Within the range from 0-8 for the 8 percent test bottle and 0-10 for the 10 percent test bottle, the maximum error in volume shall not be greater than 0.025 milliliter. The graduation marks shall be clear and fine, not more than 0.3 millimeter in width. The bottom of the bottles shall have a ground area of at least 2 square centimeters for numbering.

(b) *Water baths*.—Two water baths, as follows: A water bath maintained at 77 ± 0.5° F. (25 ± 0.3° C.) and of such depth that when a test bottle is immersed, the upper level of its contents is below the surface of the water.

A water bath maintained at 208° to 212° F. (98° to 100° C.) and of sufficient depth to permit complete immersion of the body of the test bottle.

(c) *Centrifuge*.—A centrifuge capable of whirling two or more test bottles filled with acid at a speed of 1,000 revolutions per minute. The centrifuge shall be of good design and rugged construction so that it may be operated without danger.

(d) *Burette*.—One 50-milliliter burette graduated in 0.1-milliliter divisions.

D. PROCEDURE

4. (a) 5 ± 0.1 grams of the distillate, or fraction of distillate, shall be weighed into the test bottle. If the distillate contains solid matter, the distillate shall be warmed in a hot water bath, with stirring, until the solid matter has melted before the sample for testing is taken.

(b) Then 10 milliliters of 37N H₂SO₄ shall be slowly added to the test bottle from the burette in such a way as to wash down any oil remaining in the neck of the bottle. The test bottle shall then be shaken vigorously for 2 minutes. The temperature of this acid-distillate mixture shall not be allowed to approach 212° F. (100° C.) as indicated by the bottle becoming too warm to touch, or by the contents foaming excessively. The test bottle may be cooled in ice water, if necessary. However, if the distillate contains solid matter that does not readily disperse in the acid, it may be necessary to warm the distillate-acid mixture in the hot water bath to liquefy the solid matter.

(c) An additional 10 milliliters of 37N H₂SO₄ shall be added as outlined in paragraph (b) and the bottle shaken vigorously for 30 seconds. The test bottle shall then be placed in the water bath at 208° to 212° F. (98° to 100° C.).

(d) After the test bottle has been in the bath for 10 minutes, it shall be removed, shaken vigorously for 30 seconds, and replaced immediately in the water bath at 208° to 212° F. (98° to 100° C.). If the sample boils or foams over at this stage, it shall be discarded and the test repeated.

(e) The procedure outlined in paragraph (d) shall be repeated for a total of six 10-minute immersions and shakings. After the last shaking the test bottle shall be allowed to cool.

(f) After cooling the test bottle to approximately room temperature, sufficient H_2SO_4 (specific gravity 1.84) shall be added to the contents of the test bottle to raise the liquid level in the neck to near the top of the graduation. The test bottle and its contents shall then be placed in the centrifuge and whirled at a speed of approximately 1,000 revolutions per minute for 5 minutes. The bottle shall then be removed from the centrifuge and placed in the water bath at 77° F. (25° C.) so that the upper level of its contents is below the surface of the water. After 10 minutes the test bottle shall be removed from the bath and the volume of oil read to within one-tenth of a major division. The centrifuging shall be repeated until the volume of oil is constant.

(g) Generally the unsulfonated residue is a clear transparent oil. Occasionally some white or even dark-colored solid may be present. In case solid material appears, which cannot be melted in the water bath without causing overflow in the bottle, a new test should be made. This is to be done in the same manner as previously described except that when the bottle is removed from the hot bath it should be filled immediately with H_2SO_4 (specific gravity 1.84) to a point below the top of the graduations to allow room for expansion. The bottle should then be whirled in the centrifuge for 3 minutes and again placed in the boiling water bath for 5 minutes. This cycle shall be repeated until the volume of the oil is constant. The final reading of the volume shall be made while the test bottle is immersed in the hot water bath (98° to 100° C.) and any material which is solid at this temperature (resins) shall not be included as unsulfonated residue.

(h) After a constant oil volume has been obtained by centrifuging, the reading of the bottom of the oil level shall be subtracted from the reading of the top and the difference, in terms of the major divisions, multiplied by 0.2. The value so obtained is the milliliters of unsulfonated residue in the sample. The sulfonation index is obtained by dividing the milliliters of unsulfonated residue by the weight of the sample in grams and multiplying this quotient by the percentage of distillate by weight in the tar. Thus, the sulfonation index is the milliliters of unsulfonated residue per 100 grams of tar. It shall be reported to the nearest 0.1.

E. PRECAUTIONS

5. (a) It is extremely important that all glassware used in this test shall have been thoroughly cleaned and dried before use.

(b) The required amount of vigorous shaking is very important and in no case should the designated number of shakings or the time of shaking be decreased below the limits set. It is also important that the shaking shall be such that the distillate will be completely dispersed through the acid at the conclusion of each shaking period. If excess foaming results from the shaking after any heating interval, the bottle should be cooled for 15 or 20 seconds in a cold water bath, after which the shaking can usually be continued without the contents foaming.

(c) The rate of whirling in the centrifuge may be decreased to avoid breakage of the test bottles. In all cases, however, the centrifuging shall be continued until a constant reading of the volume of unsulfonated residue is obtained.

(d) If a separate layer of sulfonation residue cannot readily be observed a more definite line of demarkation may be established by carefully adding one or two drops of water to the bottle. This sometimes calls attention to solids which, because of their color, might escape notice.

The strength of the 37N acid used in this investigation of the sulfonation index test was determined volumetrically as follows:

Approximately 2 grams of the acid were added from the burette to a weighing bottle. This was done as quickly as possible and the bottle stoppered immediately to prevent the absorption of water. The sample was weighed to the nearest 0.1 milligram, and it was then diluted with distilled water, the volume being made up to 500 milliliters. Twenty-milliliter portions of this solution were then titrated against approximately 0.1N NaOH which had been standardized against 0.1N H_2SO_4 . The strength of the dilute acid had been determined gravimetrically by precipitation with barium chloride and weighing as barium sulfate.

For use in the producers' method, acid which contains 80.07 percent SO_3 is specified and no tolerances were given. However, it is considered that a reproducibility of results better than ± 2 parts per thousand with this method cannot be obtained since this represents a burette reading of approximately 0.05 milliliter for the weights and strengths of solution mentioned. In view of this fact no effort was made to control the strength of the acid any closer than 80.1 ± 0.2 percent SO_2 (98.6 \pm 0.2 percent H_2SO_4). A refilling burette was attached to the acid bottle so that it was unnecessary to open it to the atmosphere at any time after the initial standardization. The air entering the bottle was passed through a drying tube of $CaCl_2$ to remove any moisture, and these precautions insured a satisfactory degree of constancy in the strength of the acid.

MAJORITY OF TARS TESTED OF COLD-APPLICATION TYPE

Table 6 shows the test characteristics of the tars studied in this investigation. Samples 1 through 10 were submitted for routine tests prior to 1940 and were not required to meet specifications for the sulfonation index. Samples 11, 12, and 13 were submitted by one producer for a special study, sample 11 being a "bunker C" water-gas tar, sample 12 an unrefined vertical retort tar, and sample 13 a blend of these two which was refined and marketed as RT-4. Samples 14 and 15 were submitted to meet specifications requiring a sulfonation index less than 7 on the distillate up to 300° C. and less than 1.5 on the distillate between 300° and 355° C. These two materials are from the same producer but differ in their physical properties. With the exception of sample 11, all these materials were of the cold-application grades, eight being RT-2, one RT-3, and five RT-4. Sample 11 had a consistency corresponding to RT-8.

In addition to these materials, which were studied more thoroughly, sulfonation tests were made on some samples received during the 1940-41 construction seasons. Samples 16, 18, 21, and 22 represent materials from producers or from local plants of the producers for which samples were not available in the original study.

Samples 23 through 30 represent materials supplied by one producer for one large project. Samples 23 and 24 were taken at the time of the initial delivery of the material, and samples 25 through 30 were taken later during the period of construction. The material was stored in a large tank and evidently was not agitated during the period of use, which covered several months.

In addition to the test results on the samples studied in this laboratory, data obtained by the Ohio Department of Highways in an investigation of the sulfonation index and presented to the Committee on Materials of the A. A. S. H. O. are included in this report.⁷ The tars tested in Ohio were from a majority of the producers represented in the Public Roads Administration investigation, as well as other producers, and these supplementary data provide a more general picture of the tars produced in the several localities. These data also include interesting results on several types of asphaltic products.

The results of the tests made by the Ohio Department of Highways are shown in tables 7, 8, and 9. Table 7 shows a summary of the tests on a number of tars which were marketed in Ohio. Table 8 shows the sulfonation indexes for several types of slow-curing

⁷ Appendix VI to Minutes of Meeting of Committee on Materials held March 3-4, 1941.

TABLE 6.—Physical and chemical properties of the tars examined

Sample No.	Producer No.	Engler specific viscosity at 40° C.	Specific gravity at 25° C.	Bitumen	Distillate							Residue from distillation to 300° C.	Softening point of residue		Specific gravity of distillate at 38° C.		Index of refraction of distillate at 38° C.		Sulfonation index		Volume unsulfonated residue in distillate	
					To 170° C.	170° to 200° C.	200° to 235° C.	235° to 270° C.	270° to 300° C.	300° to 355° C.	Above 300° C.		Above 355° C.	To 300° C.	300° to 355° C.	To 300° C.	300° to 355° C.	To 300° C.	300° to 355° C.	To 300° C.	300° to 355° C.	
					Percent	Percent	Percent	Percent	Percent	Percent	Percent		° C.	° C.	To 300° C.	300° to 355° C.	To 300° C.	300° to 355° C.	To 300° C.	300° to 355° C.	Percent	Percent
1	1	9.7	1.103	91.89	1.0	1.8	14.8	8.0	16.7	65.4	35.3	76.1	0.958	1.010	1.558	1.596	6.7	2.2	19.8	13.4		
2	1	10.0	1.100	90.77	1.8	10.3	13.2	7.3	15.2	66.7	34.6	73.7	.939	1.013	1.537	1.595	8.9	2.8	25.8	18.8		
3	1	9.1	1.126	92.56	1.8	10.1	11.0	7.7	13.9	68.5	40.3	73.5	.963	1.046	1.561	1.619	3.8	1.4	12.1	10.6		
4	2A	11.7	1.148	93.89	.7	12.5	13.0	6.3	11.3	65.4	45.6	69.5	1.012	1.092	1.586	1.644	.7	(3)	2.2	(3)		
5	2B	17.7	1.125	96.48	.6	19.0	11.1	6.8	13.9	71.8	37.2	60.8	.960	1.074	1.548	1.628	4.4	.3	15.5	2.3		
6	2B	23.2	1.135	96.52	.7	17.5	11.9	6.2	14.5	73.5	37.6	64.4	.969	1.074	1.551	1.630	4.4	.3	16.3	2.2		
7	1	12.1	1.118	95.32	1.4	8.2	9.7	7.0	17.9	69.8	49.2	83.0	.963	1.040	1.564	1.615	1.6	.7	5.9	4.1		
8	1	21.6	1.116	90.15	.7	.7	4.3	14.5	13.2	14.7	70.6	32.4	.949	1.019	1.548	1.598	10.4	2.5	29.8	17.5		
9	3A	24.7	1.142	93.09	.3	.7	10.2	11.4	15.2	13.6	72.1	40.4	.950	1.090	1.554	1.640	9.8	.3	24.8	2.4		
10	2C	29.9	1.174	93.07	.6	1.9	8.0	10.6	6.4	13.9	72.1	45.1	1.027	1.102	1.554	1.640	(3)	(3)	(3)	(3)		
11	4	(4)	1.177	92.55	.1	.8	3.1	6.6	6.2	15.1	82.5	51.8	83.5	.995	1.057	1.589	1.634	.4	.06	2.4	.4	
12	4	8.5	1.091	95.01	.8	1.4	6.8	11.1	8.9	18.4	69.0	31.5	61.8	.960	1.035	1.542	1.598	4.9	2.0	16.4	11.3	
13	4	35.1	1.112	95.21	.6	1.0	3.8	10.8	9.2	17.4	74.7	33.4	64.0	.966	1.036	1.551	1.603	3.9	1.6	15.0	9.6	
14	1	10.4	1.126	92.02	1.1	1.3	7.6	13.9	8.1	14.2	66.2	44.1	79.8	.975	1.046	1.570	1.621	3.6	.9	11.1	6.7	
15	1	10.8	1.118	91.70	3.2	4.6	7.2	8.2	6.2	15.9	67.4	51.0	91.0	.947	1.037	1.551	1.615	3.3	1.4	10.7	9.2	
16	5A	11.3	1.150	95.27	3.4	5.6	9.7	8.1	18.2	71.8	37.7	67.7	.948	1.037	1.551	1.615	.6	.03	10.7	9.2		
17	4	17.5	1.108	93.91	.2	1.2	5.5	11.3	8.4	15.1	70.1	38.1	63.5	.980	(5)	1.565	1.613	4.0	0	7.9	4.9	
18	3B	18.2	1.143	95.23	.6	5.6	12.4	10.6	10.6	17.4	70.6	29.9	84.7	.961	1.034	1.537	1.613	4.6	.5	11.1	6.7	
19	1	25.0	1.102	95.16	.2	.4	4.8	18.6	9.4	17.4	64.6	42.2	92.5	.939	1.029	1.537	1.613	10.5	1.3	11.1	6.7	
20	1	(5)	1.164	89.60	0	0	2.3	10.5	8.0	15.8	78.8	49.3	84.7	.961	1.034	1.537	1.613	4.2	1.4	11.1	6.7	
21	6	10.0	1.168	91.47	1.6	4.4	8.3	5.5	3.2	14.4	72.9	43.6	63.5	.980	(6)	1.565	1.613	.4	0	7.9	4.9	
22	5B	12.1	1.120	95.78	1.5	1.2	6.3	10.9	8.0	15.3	71.1	43.8	80.0	.968	1.037	1.565	1.613	2.3	.7	7.9	4.9	
23	1	12.2	1.121	91.84	2.3	3.4	7.6	9.0	7.4	17.4	69.9	44.4	94.8	.948	1.037	1.565	1.613	3.2	1.4	11.1	6.7	
24	1	11.9	1.122	95.85	2.0	2.3	8.0	11.3	6.2	14.4	67.7	47.8	80.5	.948	1.037	1.565	1.613	3.7	1.3	11.1	6.7	
25	1	10.5	1.122	92.28	1.0	.9	9.3	11.2	9.2	14.6	68.0	42.4	80.0	.968	1.037	1.565	1.613	3.8	1.1	11.1	6.7	
26	1	7.5	1.086	91.13	3.2	4.7	10.1	14.2	7.4	9.3	70.6	44.6	80.0	.968	1.037	1.565	1.613	5.3	.7	11.1	6.7	
27	1	11.6	1.116	91.76	4.1	4.4	8.2	7.7	6.9	11.1	68.0	48.2	80.0	.968	1.037	1.565	1.613	4.7	1.3	11.1	6.7	
28	1	13.9	1.119	92.33	2.2	3.4	8.8	9.4	6.7	15.1	70.2	48.2	80.0	.968	1.037	1.565	1.613	3.8	1.6	11.1	6.7	
29	1	9.6	1.110	91.45	2.2	3.7	10.5	10.2	5.8	15.1	69.8	47.7	80.0	.968	1.037	1.565	1.613	5.9	2.1	11.1	6.7	
30	1	13.1	1.113	91.85	2.8	3.6	7.6	9.2	6.4	12.1	69.8	47.7	80.0	.968	1.037	1.565	1.613	3.9	1.4	11.1	6.7	

1 Percentage of distillate from 170° to 235° C.

2 Liquid only.

3 Trace.

4 Float test at 32° C., 85 seconds.

5 Float test at 32° C., 103 seconds.

6 Fraction solid at 38° C.

7 Sample contains 12.6 percent water.

TABLE 7.—Test characteristics of road tars tested by Ohio Department of Highways

Specification grade	Producer No.	Specific gravity at 25° C.	Total bitumen	Softening point ° C.	Total distillate to 300° C.		Distillate from 300° C. to 355° C.	
					Percentage of sample	Sulfonation index	Percentage of sample	Sulfonation index
RT-2	5C	1.165	92.10	39.2	24.7	0.7	13.0	0
RT-2	5C	1.164	88.56	41.6	23.4	.8	13.2	0
RT-6	5C	1.174	95.69	37.6	21.5	.3	15.7	.1
RT-2	1	1.136	92.41	43.8	34.8	6.0	16.6	1.1
RT-2	1	1.123	92.23	47.0	34.8	6.3	15.7	1.4
RT-8	1	1.208	90.56	43.8	21.5	.7	28.3	.3
RT-6	7	1.168	91.37	53.5	21.7	.7	16.2	.1
RT-6	7	1.185	88.91	52.2	24.2	.5	13.7	.1
RT-6	7	1.183	89.43	52.0	23.8	.5	18.3	0
RT-7	7	1.167	89.90	51.6	23.1	.8	15.8	.3
RT-6	7	1.184	89.45	47.2	24.0	.8	15.0	0
RT-6	7	1.167	91.19	48.5	26.1	.7	16.6	0
RT-6	7	1.166	91.37	45.0	25.3	.9	19.1	.4
RT-6	7	1.180	89.92	49.0	25.1	.6	13.3	.1
RT-2	2D	1.135	96.36	42.8	29.5	.8	17.3	0
RT-6	2D	1.189	94.78	53.6	22.0	.1	17.2	.1
RT-5	2D	1.193	93.60	40.0	23.6	.2	16.4	0
RT-6	2C	1.187	92.22	48.6	25.2	.9	13.6	.1
RT-6	8	1.199	90.32	45.6	18.9	.2	14.4	.1
RT-6	3C	1.217	89.15	39.2	18.7	.2	14.1	.3
RT-6	3C	1.201	92.75	39.8	19.9	.1	10.9	0
RT-2	3D	1.144	95.27	35.0	32.5	2.9	13.0	0
RT-6	3E	1.207	88.84	48.4	19.4	0	13.6	.1
RT-5	3E	1.201	93.83	41.4	19.4	0	16.4	0
RT-6	3E	1.200	90.49	39.0	20.6	.4	19.3	0
RT-4	9	1.163	96.84	33.2	27.0	.1	16.4	0
RT-4	9	1.164	95.06	35.0	28.9	.2	19.3	0
RT-2	10	1.161	95.63	32.0	25.8	.2	16.4	0

TABLE 8.—Sulfonation indexes of various types of slow-curing liquid asphaltic road materials

[Tests made by Ohio Department of Highways]

Sample identification	Specific gravity at 25° C.	Xylene equivalent	Total distillate to 300° C.		Distillate from 300° to 355° C.	
			Percentage of sample	Sulfonation index	Percentage of sample	Sulfonation index
W	1.001	83-85	15.2	6.4	21.9	6.7
X	1.044	100+	20.8	3.9	23.2	4.4
Y	1.006	100+	17.8	7.8	19.1	6.1
Z	.917	0	12.7	11.4	36.1	27.7

TABLE 9.—Effect of blending an asphaltic product with a tar on its test characteristics

[Tests made by Ohio Department of Highways]

Test	RT-2	SC-O	Blend 1
Specific gravity at 25° C.	1.165	1.052	1.118
Total bitumen soluble in CS ₂	92.10	99.68	97.02
Solubility in CCl ₄	98.68	64.9	98.68
Amount of 100 penetration residue	31.0	143	31.0
Total distillate to 360° C. ²	24.7	20.8	26.0
Float of residue at 50° C.	39.2	39.2	35.0
Softening point of residue	39.2	23.2	13.4
Distillate from 300-355° C.	13.3	3.9	3.3
Sulfonation index, distillate to 300° C.	.7	4.4	1.4
Sulfonation index, distillate 300-355° C.	0	4.4	1.4

1 Blend contains 65 percent of the RT-2 and 35 percent of the SC-O.

2 Method A. S. T. M. D402-36.

3 Method A. S. T. M. D20-30.

liquid asphaltic road materials and table 9 shows test results obtained with a tar of the RT-2 grade, one of the slow-curing asphaltic materials, and a blend of these two.

An examination of tables 6 and 7 will show that almost all of the tars having high sulfonation indexes were received from producer No. 1, while samples from plants A, B, and D of producer No. 3 had considerable unsulfonated residue in the portion of the distillate up to 300° C. but very little in the portion between 300° and 355° C. Some samples from producer No. 4, which contained vertical retort tar also had an appreciable amount of unsulfonated residue. The unsulfonated residues from the 300° to 355° C. fractions of these samples were peculiar in that they were solid at room temperature.

Table 8 serves to illustrate the amount of unsulfonated residue in various types of slow-curing liquid asphaltic road materials, and the effect of cracking on the sulfonation index. Those samples having high xylene equivalents have much lower indexes than do the materials which react negatively in the spot test. Table 9 is very interesting since it shows that tars having low sulfonation indexes can be blended with appreciable percentages of certain cracked petroleum products without exceeding the proposed limits for the sulfonation index.

SUBSTITUTE TESTS FOUND UNSATISFACTORY

Since the sulfonation index test requires the use of extensive laboratory equipment and is a somewhat complicated procedure requiring carefully controlled reagents, attention was given to the possibility of developing a substitute test that would give comparable results. In 1913, Reeve and Lewis made a study of the dimethyl sulfate test as a means for determining approximately the amounts of petroleum products in the tar-oil or tar-asphalt mixtures.⁸ This test depends on the selective solubility of the various hydrocarbons in dimethyl sulfate in which the aromatic and unsaturated, or olefinic hydrocarbons, and their derivatives are considered to be completely soluble, and the paraffinic and naphthenic essentially insoluble. The test is made by shaking 6 milliliters of dimethyl sulfate with 4 milliliters of distillate in a 10-milliliter graduate and reading the volume of insoluble distillate which settles out. This amount is considered to be the paraffinic and naphthenic hydrocarbons. Since dimethyl sulfate is very poisonous some study has been made of the use of the less poisonous diethyl sulfate as a substitute.

J. N. Taylor⁹ investigated the use of this material and developed a method whereby he used 5 milliliters of a petroleum oil (completely immiscible with diethyl sulfate), 5 milliliters of distillate, and 16 milliliters of diethyl sulfate. The petroleum oil was added to repress the solubility of the distillate in the diethyl sulfate, and by this method he found it possible to check closely with the amount of unsulfonated material in a synthetic mixture of petroleum oil and benzenes. He also found close agreement between this test and the sulfonation residue for the distillate obtained from "dips." In view of the success of these methods for the purposes of these authors, it was decided to investigate both these

⁸ Application of the Dimethyl Sulfate Test for Determining Small Amounts of Petroleum or Asphalt Products in Tars. Journal Industrial Chemistry, vol. 5, No. 3, 1913.

⁹ Dimethyl Sulfate in the Examination of Hydro-Carbon Oils, by J. N. Taylor. Industrial and Engineering Chemistry, vol. 19, June 1927.

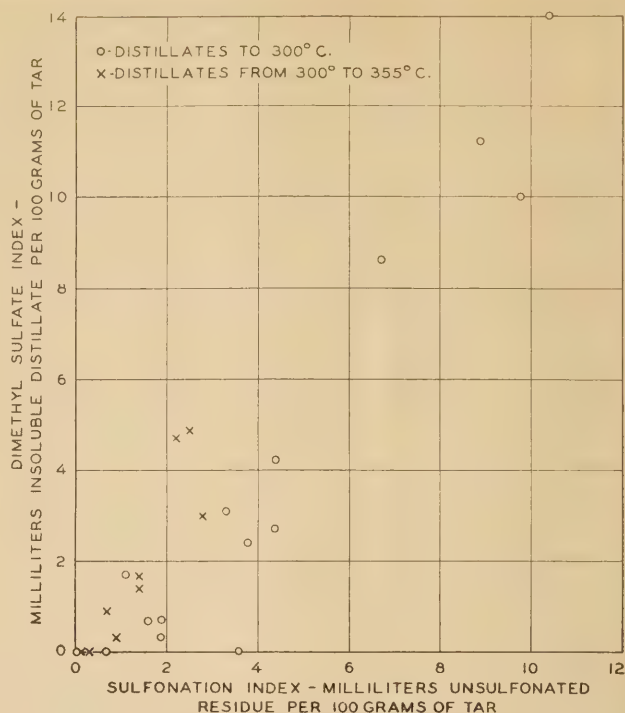


FIGURE 1.—RELATION BETWEEN DIMETHYL SULFATE INSOLUBLE AND SULFONATION INDEX.

methods for use as a substitute for the sulfonation index test on tar distillates.

The dimethyl sulfate test was made on a number of the samples for which the sulfonation index was determined. The results of these tests are shown in table 10. These tests were made at room temperature as were those by Reeve and Lewis.⁸ It is seen that there was not good agreement between the values obtained by the two methods, nor was there a definite relationship between the two values. This is illustrated in figure 1, in which the sulfonation index is plotted against the dimethyl sulfate index. An attempt was made to discover a relationship by varying the proportions of dimethyl sulfate to distillate and also by varying the temperature. These tests were made on the distillate from sample 2, and the results are shown in table 11.

TABLE 10.—Comparison of distillate insoluble in dimethyl sulfate with amount of unsulfonated residue

Sample No.	Distillate to 300° C.				Distillate from 300° to 355° C.			
	Sulfonation index	Dimethyl sulfate index	Volume of unsulfonated residue	Volume insoluble in dimethyl sulfate	Sulfonation index	Dimethyl sulfate index	Volume of unsulfonated residue	Volume insoluble in dimethyl sulfate
1	6.7	8.6	Percent 19.8	Percent 25.0	2.2	4.7	Percent 13.4	Percent 32.0
2	8.9	11.2	25.8	32.0	2.8	3.0	18.8	28.0
3	3.8	2.4	12.1	7.0	1.4	1.4	10.6	10.0
4	.7	0	2.2	0	(¹)	0	(¹)	0
5	4.4	4.2	15.5	15.0	.3	0	2.3	0
6	4.4	2.7	16.3	10.0	.3	0	2.2	0
7	1.6	.7	5.9	3.0	.7	.9	4.1	5.0
8	10.4	14.0	29.8	40.0	2.5	4.9	17.5	34.0
9	9.8	10.0	24.8	25.0	.3	(¹)	2.4	(¹)
10	(¹)	0	(¹)	0	0	0	0	0
14	3.6	(¹)	11.1	(¹)	.9	.3	6.7	2.0
15	3.3	3.1	10.7	10.0	1.4	1.7	9.2	11.3

¹ Trace.

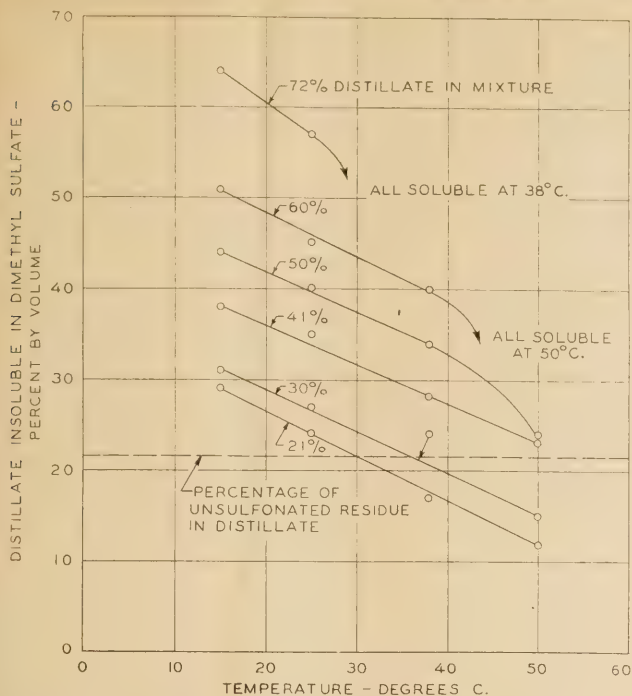


FIGURE 2.—VARIATION OF PERCENTAGE OF DISTILLATE INSOLUBLE IN DIMETHYL SULFATE WITH TEMPERATURE AND PROPORTIONS OF THE DISTILLATE IN THE TEST SOLUTION. DISTILLATE UP TO 300° C. FROM SAMPLE 2.

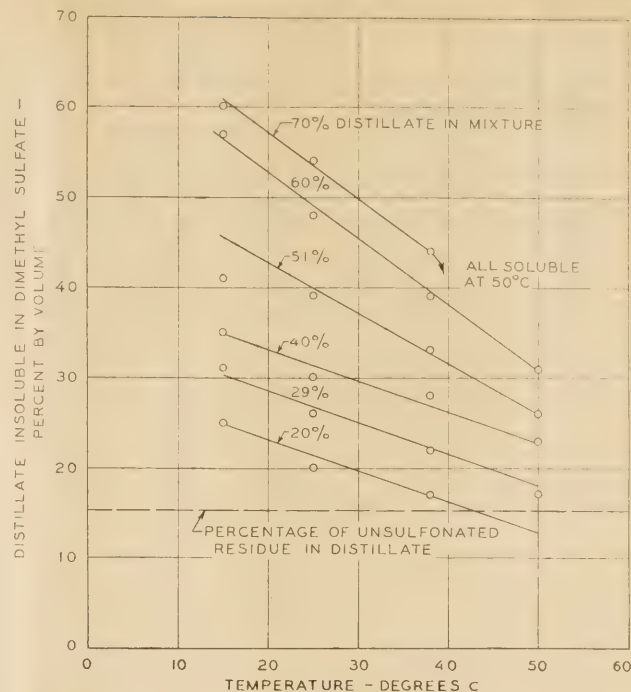


FIGURE 3.—VARIATION OF PERCENTAGE OF DISTILLATE INSOLUBLE IN DIMETHYL SULFATE WITH TEMPERATURE AND PROPORTIONS OF THE DISTILLATE IN THE TEST SOLUTION. DISTILLATE BETWEEN 300° AND 355° C. FROM SAMPLE 2.

Figures 2 and 3 show the temperature plotted against the percent insoluble for each proportion. Figure 2 represents the data for the distillate up to 300° C. and figure 3 represents that for the distillate between 300° and 355° C. These results showed that variations in either the temperature or the proportions of dimethyl sulfate and distillate made large differences in the results. Tests were then made with distillate fractions from sample 2, as shown in table 12 and plotted in figure 4. These results again showed no general relationship and the percent insoluble which was equal to the amount of unsulfonated residue was obtained at widely different temperatures.

TABLE 11.—The effect of temperature and proportion of solvent on the solubility of tar distillates in dimethyl sulfate (DISTILLATE TO 300° C. (21.5 PERCENT BY VOLUME UNSULFONATED))

Volume of distillate in mixture	Volume of distillate insoluble in dimethyl sulfate at—				
	15° C.	25° C.	Room temperature ¹	38° C.	50° C.
Percent	Percent	Percent	Percent	Percent	Percent
21	29	24	17	17	12
30	31	27	20	24	15
41	38	35	26	28	23
50	44	40	34	34	24
60	51	45	37	40	0
72	64	57	---	0	0

DISTILLATE FROM 300° TO 355° C. (15.2 PERCENT BY VOLUME UNSULFONATED)					
Percent	Percent	Percent	Percent	Percent	Percent
20	25	20	15	17	17
29	31	26	24	22	17
40	35	30	30	28	23
51	41	39	36	33	26
60	57	48	43	39	31
70	60	54	45	44	0

¹ Room temperature approximately 32° C.

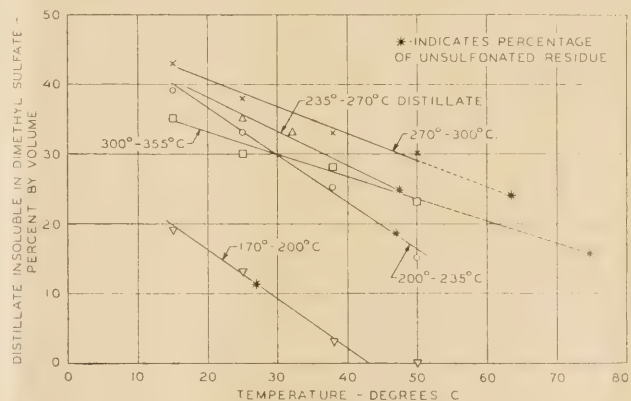


FIGURE 4.—VARIATION OF PERCENTAGE OF DISTILLATE INSOLUBLE IN DIMETHYL SULFATE WITH TEMPERATURE FOR VARIOUS FRACTIONS DISTILLED FROM SAMPLE 2.

TABLE 12.—The effect of temperature on the solubility of the various distillation fractions of a tar in dimethyl sulfate

Distilling temperature of fraction	Volume of unsulfonated residue	Volume of distillate insoluble in dimethyl sulfate at—				
		15° C.	25° C.	Room temperature ¹	38° C.	50° C.
° C.	Percent	Percent	Percent	Percent	Percent	Percent
170-200	11.4	19	13	8	3	0
200-235	18.5	39	33	25	25	15
235-270	24.9	---	35	33	---	---
270-300	23.8	43	38	35	33	30
300-355	15.2	35	30	30	28	23

¹ Room temperature approximately 32° C.

When diethyl sulfate was substituted for the dimethyl sulfate, using the same procedure as used for the dimethyl sulfate tests, no insoluble could be obtained even for distillates containing very high percentages

of unsulfonated residue. Accordingly, Taylor's⁹ method was tried. There was some difficulty in finding a petroleum oil that was completely immiscible with diethyl sulfate and at the same time had a low viscosity so that accurate volumetric measurements could be made. After experimentation, kerosene which had been sulfonated to remove all aromatic and unsaturated compounds was chosen as being the best material easily available. It was discovered, however, that there was a slight mutual solubility of the kerosene and diethyl sulfate. Thus, in order to obtain more accurate results, the kerosene was saturated with diethyl sulfate and the diethyl sulfate was saturated with kerosene. Using these precautions, tests similar to those with the dimethyl sulfate were made. The test temperature and proportions of solute and solvent were varied. The same general result was obtained and no relationship could be established.

These results show clearly that neither of these tests can be correlated with the sulfonation index test, nor can they be used as a test method for specification requirements. They are at best qualitative tests and can be used only as an indication of the presence of large amounts of paraffinic hydrocarbons.

RELATIONSHIP BETWEEN SPECIFIC GRAVITY OF DISTILLATE AND SULFONATION INDEX STUDIED

The relationship of the softening points of the distillation residues from both the distillation to 300° C. and the distillation to 355° C. to the amount of unsulfonated residue in the distillate was examined and no definite trend was found.

The specific gravity at 38° C. of the distillate was also determined and compared to the sulfonation index. No straight-line relation was found but there is a definite minimum value for the specific gravity above which the sulfonation index is always lower than the requirements in the proposed specifications. When the specific gravity is below this minimum, the sulfonation index is usually high. However, in some cases a low sulfonation index was found in conjunction with a low specific gravity.

These results are in accordance with the well-known fact that, for the same boiling point range, the specific gravities of the aromatic hydrocarbons are higher than those of the unsaturated compounds which, in turn, have higher gravities than the paraffinic materials. The specific gravities of the naphthenic group, however, fall between those of the unsaturated and aromatic groups. Thus, the specific gravity of a mixture containing the maximum specified amount of unsulfonated residue is greatest when this unsulfonated residue is naphthenic and the sulfonated portion is aromatic. This value of the specific gravity theoretically represents the minimum above which the sulfonation index is always less than the specified maximum. The converse is not true since the presence of the olefinic group which is readily sulfonated may lead to combinations of widely different percentages of unsulfonated hydrocarbons having the same specific gravity. Thus, if this "critical" specific gravity can be determined, a clause could be inserted in the specifications stating that if the specific gravity of the distillate is greater than this value the material is acceptable. However, if the specific gravity is less than this value, the sulfonation index must be determined.

⁹ Diethyl Sulfate in the Examination of Hydro-Carbon Oils, by J. N. Taylor. Industrial and Engineering Chemistry, vol. 19, June 1927.

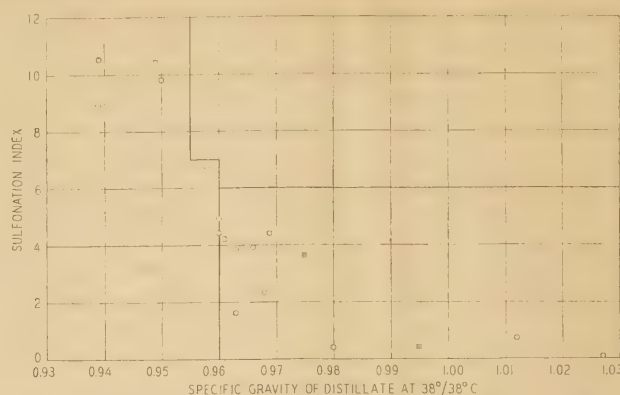


FIGURE 5.—RELATION BETWEEN THE SULFONATION INDEX AND THE SPECIFIC GRAVITY OF THE 0°–300° C. FRACTIONS.

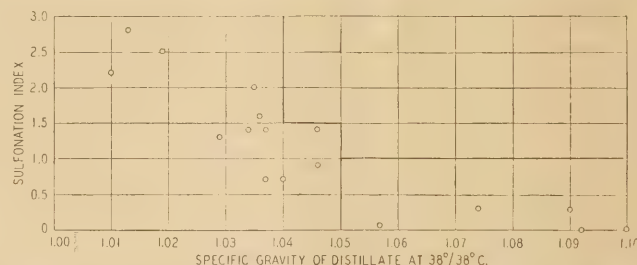


FIGURE 6.—RELATION BETWEEN THE SULFONATION INDEX AND THE SPECIFIC GRAVITY OF THE 300°–355° C. FRACTIONS.

Figures 5 and 6 show the sulfonation index plotted against the specific gravity of the distillate at 38°/38° C., figure 5 representing the data for the distillate up to 300° C. and figure 6 representing the data for the distillate between 300° and 355° C. These data were recorded in table 6. It is seen from the figures that for the materials tested, all samples of distillate to 300° C. which had a specific gravity at 38°/38° C. of 0.960 or more, had a sulfonation index less than 6. However, two of the distillates to 300° C. reported in table 6 had specific gravities lower than 0.960 and sulfonation indexes less than 6. Likewise, all samples having a specific gravity at 38°/38° C. of 0.955 or more, had sulfonation indexes less than 7. For the distillate from 300° C. to 355° C. this critical specific gravity is 1.05 at 38° C. for a sulfonation index of 1.0, and 1.04 at 38° C. for a sulfonation index of 1.5. However, 4 samples of the distillate between 300° C. and 355° C. which had specific gravities at 38° C. of less than 1.04 had sulfonation indexes less than 1.5, and 3 samples which had specific gravities at 38° C. of less than 1.05 had sulfonation indexes less than 1.0.

TARS AND SAND-TAR MIXES EXPOSED IN WEATHEROMETER

It should be pointed out that these figures represent the results for the samples tested by this laboratory and it is possible that tars from other sources, or those having unusually large amounts of distillate, might have slightly higher specific gravities than these values and still exceed the maximum values for the sulfonation index by small amounts. Nevertheless, it is apparent from the above discussion that under certain conditions it should be possible to eliminate the necessity of making a large number of sulfonation index determinations on road tars by establishing suitable "critical" values for the specific gravities of the distillates.

In order to correlate, if possible, the weathering

properties of the tars with the amount of unsulfonated residue, two series of accelerated exposure tests were made in the weatherometer (see cover illustration) using thin films of the tars and molded sand mixes containing the tar.

The tars were exposed in seamless flat tins 5½ inches in diameter and ¾-inch deep which, when filled with 50 milliliters of tar, give the desired film thickness of ⅛ inch.

The mixes were made in the same proportions and with the same type of sand as in the work done by Lewis and Welborn in their study of road tars.¹⁰ The mixes contained 16.6 percent by volume of tar, and the sand had a grading as shown in table 13.

Two sizes of cylinders were molded, one size 2 inches in diameter and 1 inch high for Hubbard-Field stability tests, and the other 1 inch in diameter and 1 inch high for toughness tests with the Page impact machine.

TABLE 13.—Grading of sand in mixes on which accelerated exposure tests were made

Passing sieve—	Retained on sieve—	Percent
No. 10	No. 20	3.7
No. 20	No. 30	10.3
No. 30	No. 40	18.1
No. 40	No. 50	21.3
No. 50	No. 80	36.6
No. 80	No. 100	6.1
No. 100	No. 200	3.2
No. 200		.7

The cylinders were molded at 3,000 pounds per square inch, the load being released immediately (single plunger method). The initial stability and impact were determined for all mixes immediately after molding.

The weatherometer was controlled at 60° C. and approximately 50 percent humidity, a dry cycle being used entirely. One group of samples, which consisted of one sample of tar and two of each size cylinder, was removed at the end of 60 hours exposure, the second after 200 hours, and the third after 400 hours. The percentage of loss, specific gravity at 25° C. and kinematic viscosity at several temperatures were determined for each of the residues from the tar samples, and the percentage of loss, stability at 25° C., and impact were determined for the sand-tar mixes.

In the first series, samples 1 through 10, with the exception of sample 5, were tested, and in the second series samples 11 through 15 were tested. It should be noted that for 20 hours between the 60- and 200-hour periods a blown fuse in the line operating the cooling fan caused the overheating of the samples in series 2 to approximately 95° C. For this reason these samples generally show a greater loss and more hardening than do those of the first series.

Table 14 shows the rate of loss of volatile matter for the tar samples in both series. These data are computed in three different ways for comparison. The loss of the sample, the loss of the distillate (based on the total distillate to 300° C.), and the proportion of the total loss are shown for each exposure period. Two results are given for each sample—one, the value for the 400-hour sample at the end of each period, and the other the value for the sample removed from the weatherometer at the end of each intermediate time interval.

¹⁰ A Study of Road Tars, by R. H. Lewis and J. Y. Welborn. PUBLIC ROADS, vol. 17, No. 5, July 1936.

It is of interest to note two different types of behavior with these samples. Samples of one type formed a dull surface skin in a comparatively short time, and samples of the other type remained glossy until very near the end of the 400-hour test period. Samples 1, 2, 3, 7, 8, 14, and 15 exhibited the first type of behavior, and samples 4, 6, 9, and 10 exhibited the second type. Samples 11, 12, and 13 are of special interest since they are from known sources. Sample 11, the "bunker C" water-gas tar, had developed a dull and wrinkled skin by the end of 200 hours, while sample 12, the vertical retort tar, hardened greatly and developed a greasy black surface without any evidence of a surface skin. Sample 13, the blend of the two, exhibited both types of surface. It had a dull skin over most of the surface and wherever this skin had parted the exposed portion was very similar in appearance to the surface of sample 12.

TABLE 14.—Rate of loss of volatile matter in thin-film exposures of tar samples in the weatherometer

Sample No. 1	Loss of sample after—			Loss of total distillate 2 after—			Proportion of total loss after—		
	60 hours	200 hours	400 hours	60 hours	200 hours	400 hours	60 hours	200 hours	400 hours
	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
1(a)	28.3	28.7	29.0	82	83	84	98	99	100
1(b)	28.4	29.0		82	84		98	100	
2(a)	28.2	28.6	29.1	85	86	87	97	98	100
2(b)	28.0	28.4		84	85		96	98	
3(a)	25.0	25.2	25.6	79	80	81	98	98	100
3(b)	25.0	25.4		79	81		98	99	
4(a)	25.3	28.4	28.7	73	82	83	88	99	100
4(b)	25.2	29.2		73	84		88	102	
6(a)	22.4	23.7	24.1	85	89	91	93	98	100
6(b)	22.5	24.2		85	91		93	100	
7(a)	22.6	23.2	23.6	75	77	78	96	98	100
7(b)	22.6	23.3		75	77		96	99	
8(a)	25.5	25.9	26.2	87	88	89	97	99	100
8(b)	25.5	25.9		87	88		97	99	
9(a)	21.3	24.0	24.4	72	81	82	87	98	100
9(b)	21.2	24.8		71	84		87	102	
10(a)	20.1	22.5	22.7	72	81	81	89	99	100
10(b)	20.4	20.0		73	72		90	88	
11(a)	6.9	10.8	10.8	39	62	62	64	100	100
11(b)	7.2	10.9		41	62		67	101	
12(a)	34.8	40.8	43.3	112	132	140	80	94	100
12(b)	28.9	34.9		93	113		67	81	
13(a)	22.0	27.2	27.6	87	108	109	80	99	100
13(b)	21.9	27.0		87	107		79	98	
14(a)	27.1	31.2	31.2	80	92	92	87	100	100
14(b)	26.7	30.7		79	91		86	98	
15(a)	23.6	27.3	27.3	72	84	84	86	100	100
15(b)	23.6	27.2		72	82		86	100	

¹ Figures in line a are for 400-hour residues at the designated time interval. Figures in line b are for the residues removed from the weatherometer at the designated time interval.

² As determined by A. S. T. M. distillation test to 300° C.

The results of all the tests on the tar residues from the weatherometer are shown in table 15. The kinematic viscosity data were plotted on the A. S. T. M. viscosity-temperature chart (high range) in order to obtain the viscosity-temperature susceptibility (V. T. S.) coefficient, which is the tangent of the angle that the plotted line makes with the temperature axis. A difference of 1 degree in the angle makes a difference of approximately 0.07 in the V. T. S. coefficient. Thus it is seen from the values reported that generally all of the lines for each sample were parallel or very nearly so, and in all cases where there was a difference the V. T. S. coefficient was smaller for the longer exposure periods.

"HARDENING INDEX" OFFERS MEANS OF COMPARING DEGREE OF HARDENING

Since there is such a small difference in the susceptibility of the various residues, the viscosity-temperature lines may be considered parallel, which means that the

difference between the double logarithms of the viscosities of two residues is a constant at different temperatures. The magnitude of this difference is also a measure of the amount of hardening in a sample. Thus, for comparing the viscosities of a group of samples, the double logarithm of the kinematic viscosity at the temperature desired, multiplied by 100 for convenience, may be considered a "viscosity coefficient" for that temperature, and the difference between the "viscosity coefficients" for any two residues from the same sample is a measure of the amount of hardening which has taken place. This viscosity coefficient at 50° C., and the difference between the coefficients for the 200- and 60-hour residues, and the difference between the 400- and 200-hour residues are also shown in table 15.

TABLE 15.—Results of tests on the residues after exposure in the weatherometer

Sample No.	Time exposed		Loss	Specific gravity at 25° C.	Kinematic viscosity at				V. T. S. coefficient	Viscosity coefficient at 50° C.	Change in viscosity coefficient
					35° C.	50° C.	65° C.	82° C.			
	Hours	Percent		Stokes	Stokes	Stokes	Stokes				
1	60	28.4	1.169	6,070	265	38.2	0.93	64.6			
	200	29.0	1.174	1,880	121	18.5	.93	72.2		7.6	
	400	29.0	1.178	6,660	274	32.5	.93	76.5		4.3	
2	60	28.0	1.179	9,580	415	51.2	.97	66.4			
	200	28.4	1.183	2,680	152	22.4	.97	73.5		7.1	
	400	29.1	1.186	10,100	491	43.6	.97	77.8		4.3	
3	60	25.0	1.192	2,950	222	40.8	.90	63.8			
	200	25.4	1.198	926	92.4	17.3	.87	69.6		5.8	
	400	25.6	1.201	2,440	226	32.9	.87	73.1		3.5	
4	60	25.2	1.220	2,870	175	23.1	1.03	62.8			
	200	29.2	1.229	2,080	143	18.0	1.00	72.6		9.8	
	400	28.7	1.233	3,750	253	30.0	.97	74.6		2.0	
6	60	22.5	1.200	8,330	372	36.0	1.07	66.0			
	200	24.2	1.207	1,760	114	13.3	1.03	72.0		6.0	
	400	24.1	1.209	2,400	163	17.4	1.03	73.1		1.1	
7	60	22.6	1.182	3,050	241	34.2	.93	64.2			
	200	23.3	1.188	1,210	121	20.9	.84	70.6		6.4	
	400	23.6	1.191	2,650	245	37.7	.84	73.5		2.9	
8	60	25.5	1.187	9,100	547	70.4	.93	67.6			
	200	25.9	1.189	2,390	195	29.9	.90	73.1		5.5	
	400	26.2	1.189	5,810	430	50.0	.90	76.1		3.0	
9	60	21.2	1.213	4,500	254	32.1	1.02	64.4			
	200	24.8	1.226	2,010	154	20.4	.95	72.5		8.1	
	400	24.4	1.231	2,750	233	27.0	.95	73.6		1.1	
10	60	20.4	1.224	5,620	279	31.0	1.07	64.8			
	200	20.0	1.233	1,950	128	18.1	.95	72.3		7.5	
	400	22.7	1.233	2,310	155	22.8	.93	72.9		.6	
11	60	7.2	1.201	4,270	321	48.5	.92	65.4			
	200	10.9	1.212	5,310	457	58.1	.88	75.8		10.4	
	400	10.8	1.214	8,790	707	70.9	.88	77.4		1.6	
12	60	28.9	1.153	1,550	105	13.6	1.09	60.4			
	200	34.9	1.174	7,640	346	36.8	1.09	77.0		16.6	
	400	43.3	1.186	175,000	4,880	258	1.04	86.0		9.0	
13	60	21.9	1.162	6,010	352	39.1	1.02	65.8			
	200	27.0	1.179	7,890	456	46.5	1.98	77.1		11.3	
	400	27.6	1.178	17,560	815	81.1	.98	79.6		2.5	
14	60	26.7	1.188	2,170	181	29.9	.90	62.9			
	200	30.7	1.196	2,960	271	36.5	.88	73.8		10.9	
	400	31.2	1.200	6,420	536	65.3	.88	76.4		2.6	
15	60	23.6	1.179	2,960	230	39.3	.92	64.0			
	200	27.2	1.190	4,330	362	50.2	.82	75.1		11.1	
	400	27.3	1.193	6,730	560	72.6	.82	76.6		1.5	

In some cases greater deviations from a straight line were obtained when the data were plotted on the A. S. T. M. viscosity-temperature chart than could be attributed to experimental error. This is believed to have been caused by a large amount of carbon particles in the residue which introduced plastic or nonuniform flow in the tube of the viscosimeter. The nonhomogeneity of these residues was also indicated by their dull or grainy appearance when stirred. In several

instances, with the 60-hour residues from samples 2 and 7, there was a separation of a very small amount of clear oil on the top of the rising column of tar during the progress of the viscosity determination. This occurred during the first determination on the residue from sample 2 at 50° C. and at 65° C. For sample 7 it occurred during the first determination at 50° C. This separation always resulted in an abnormally low viscosity value which had to be discarded.

Generally these irregularities occurred with the residues from samples having high sulfonation indexes, while the residues from samples having low sulfonation indexes usually showed very little deviation from the straight line. However, sample 7, which had a low sulfonation index, exhibited these irregularities. In general appearance and test results this sample was very similar to those having high sulfonation indexes, while on the other hand sample 9, which had a very high sulfonation index on the distillate up to 300° C. but a low index on the distillate from 300° to 355° C., exhibited properties similar to the tars having low sulfonation indexes in both cases. These exceptions to the general behavior show how difficult it is to correlate the behavior of the road tar with its content of paraffinic hydrocarbons, or to set up a requirement for the sulfonation index that will definitely distinguish between tars that will be satisfactory in service and those that will be unsatisfactory.

Since tars lose their volatile constituents very rapidly in the weatherometer, the results of the tests shown in table 14 give no indication of the drying characteristics of the tars. In order to gain some knowledge of the changes in the physical properties of the tars during the drying period, a special study of samples 2, 3, and 4 was made. As is shown in table 6, these samples have almost the same viscosity, percentage of bitumen, and percentage of distillate to 300° C. The sulfonation indexes, however, differ greatly. Sample 2 has indexes of 8.9 for the distillate up to 300° C. and 2.8 for the distillate between 300° and 355° C., which exceed all the proposed specification limits. Sample 3 has indexes of 3.8 for the 0°-300° C. fraction and 1.4 for the 300° to 355° C. fraction, which are slightly lower than the maximum values proposed in some specifications. Sample 4 has very low sulfonation indexes—0.7 on the distillate up to 300° C. and a trace on the distillate from 300° to 355° C.

Three distillations were made for each of these tars, one up to 240° C., one to 270° C., and the third up to 300° C. In order further to compare the physical properties of these materials, the volume of the distillate and the liquid temperature were recorded for each 10° C. interval of vapor temperature. These distillations were made using the standard distillation apparatus. The specific gravity and the weight of the distillate from each distillation were determined and each residue was tested for kinematic viscosity at 50° C. and specific gravity at 25° C. The distillation data are plotted in figure 7 and it is seen that these samples have comparable volatility. The results of the tests on the distillates and the residues are shown in table 16. This table also includes a "hardening index" which is explained in the following discussion.

As stated previously, the viscosity coefficient may be represented by the double logarithm of the kinematic viscosity in centistokes multiplied by 100. This figure is an index of the consistency of the material at any

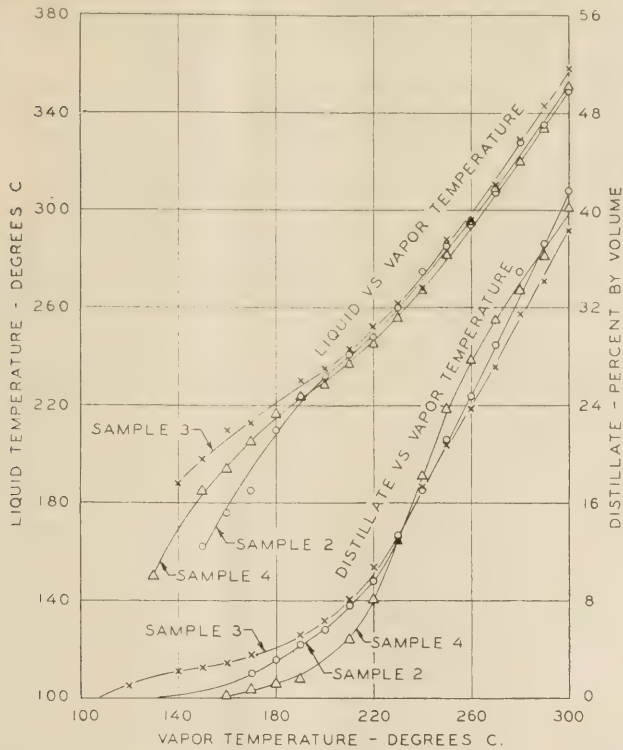


FIGURE 7.—RELATIONS BETWEEN THE LIQUID AND VAPOR TEMPERATURES, AND BETWEEN THE VOLUME OF DISTILLATE AND VAPOR TEMPERATURE.

particular time, but has no connection with the original consistency of the material or the percentage of loss. The hardening (increase in viscosity) of any material may be caused by evaporation losses or by chemical and physical changes within the tar itself, such as oxidation or polymerization, or by a combination of both factors. The first of these causes is a necessary property of liquid road materials and for rapid setting up should be as high as possible, while the hardening from changes within the structure of the tar itself should be as low as possible if the tar is to retain its life for a long period of time. Thus it is very desirable to establish the proportion of the hardening which should be attributed to evaporation losses and the proportion which should be attributed to other changes.

TABLE 16.—Properties of the residues and distillates from selected tars distilled to various temperatures

Sample No.	Highest distillation temperature	Specific gravity of residue at 25° C.	Specific gravity of distillate at 38° C.	Weight of distillate	Volume of distillate	Kinematic viscosity of residue at 50° C.	Viscosity coefficient of residue at 50° C.	Hardening index
2	° C.	1.100		Percent	Percent	Centistokes		
	240	1.137	0.912	14.3	16.7	564	44.0	1.32
	270	1.172	.930	26.5	31.0	6,320	58.0	1.28
	300	1.201	.940	34.9	40.7	105,000	70.1	1.32
3		1.126		0		44.5		
	240	1.168	.935	15.8	18.5	1,360	49.6	1.77
	270	1.193	.952	25.2	29.5	14,200	61.8	1.59
	300	1.217	.965	33.1	38.5	199,000	72.4	1.53
4		1.148		0		46.5		
	240	1.202	.992	19.5	22.5	1,770	51.2	1.49
	270	1.228	1.004	29.2	33.2	41,700	66.5	1.52
	300	1.245	1.013	35.6	40.6	831,000	77.2	1.55

TARS WITH HIGHEST SULFONATION INDEXES SHOW GREATEST "INTERNAL HARDENING"

The distillation test is conducted under conditions which should give the hardening caused by loss of volatile portions alone. It was found that when the viscosity coefficients at 50° C. were plotted as ordinates and the percentage of loss by weight in obtaining the distillation residues were plotted as abscissae, a close approximation to a straight line was obtained. The slope of this line represents the average amount of hardening for 1 percent of loss in the distillation test. It is a measure of hardening and is called the hardening index. However, in order to obtain a definite numerical value, the hardening indexes shown in tables 16 and 17 were calculated by the following equation:

$$HI = \frac{V_1 - V_0}{W}$$

where

- HI = hardening index,
- V₁ = viscosity coefficient at 50° C. of the residue,
- V₀ = viscosity coefficient at 50° C. of the sample, and
- W = percentage of loss by weight in obtaining the residue.

It is noted that the values of the hardening index shown in table 16 are very nearly constant except for the distillation to 240° C. for sample 3, and this difference is probably due to experimental error.

The hardening characteristics of the three samples in the weatherometer were determined by exposing the tars in the usual 1/8-inch films for periods of 2, 4, 8, 16, 32, 64, and 128 hours. The residues from each of these periods were weighed to obtain the percentage of loss. The kinematic viscosity at 50° C. and the specific gravity at 25° C. were also determined. The hardening index for each residue was calculated. All these results are shown in table 17.

TABLE 17.—Properties of the residues from selected tars exposed in the weatherometer

Sample No.	Time exposed	Specific gravity of residue at 25° C.	Loss in weight	Kinematic viscosity at 50° C.	Viscosity coefficient at 50° C.	Hardening index
2	Hours		Percent	Centistokes		
	0	1.100	0	55.8	24.1	
	2	1.128	11.9	285	39.0	1.25
	4	1.140	16.3	753	45.9	1.34
	7	1.151	20.4	1,930	51.7	1.35
	16.5	1.164	24.5	6,550	58.2	1.39
	32	1.172	27.0	22,500	63.9	1.47
	64	1.179	28.7	71,800	68.6	1.55
	128	1.181	28.6	220,000	72.8	1.70
	400	1.183	28.4	268,000	73.5	1.74
3	0	1.126	0	44.5	21.7	
	2	1.152	11.5	264	38.4	1.45
	4	1.160	14.2	501	43.1	1.51
	7	1.169	18.2	1,280	49.3	1.51
	16.5	1.180	22.3	4,940	56.7	1.57
	32	1.187	24.4	12,800	61.3	1.62
	64	1.192	25.2	28,400	64.9	1.71
	128	1.195	25.2	53,200	67.5	1.81
	200	1.198	25.4	92,700	69.6	1.89
	400	1.201	25.6	244,000	73.1	2.01
4	0	1.148	0	46.5	22.2	
	2	1.180	10.8	265	38.4	1.50
	4	1.188	14.3	538	43.6	1.50
	7	1.197	17.6	1,260	49.1	1.53
	16.5	1.207	21.5	4,330	56.1	1.57
	32	1.214	24.2	13,700	61.7	1.63
	64	1.220	26.5	36,200	65.9	1.65
	128	1.224	28.4	133,000	71.0	1.72
	200	1.229	29.2	208,000	72.6	1.73
	400	1.233	28.7	375,000	74.6	1.83

¹ Results from tests made in series 1; also shown in table 15.

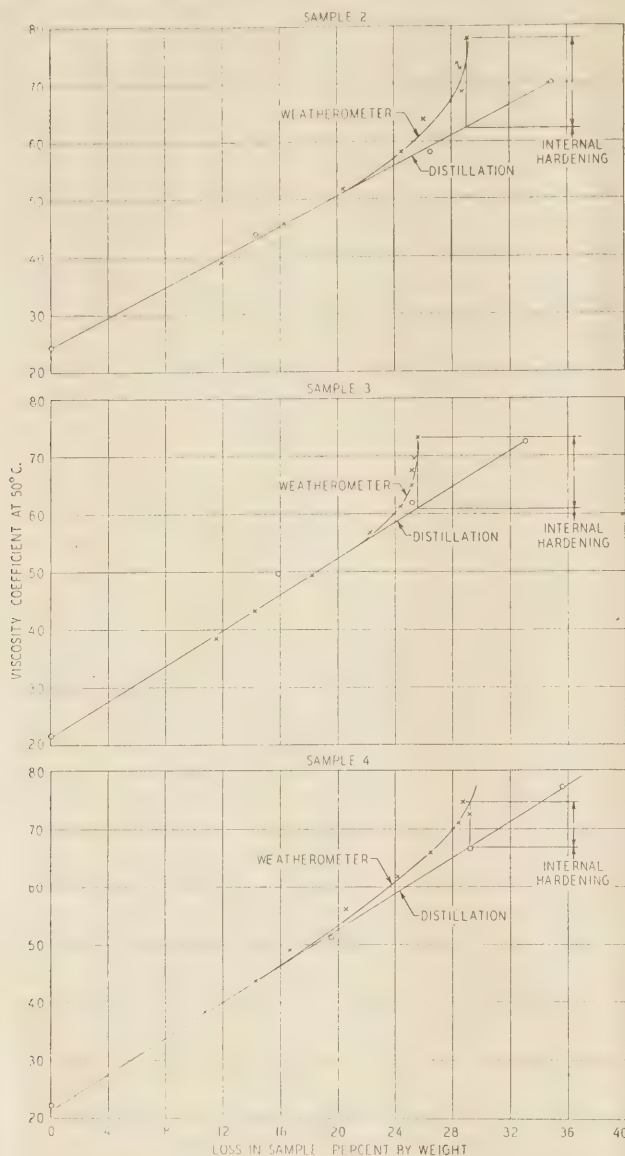


FIGURE 8.—RELATION BETWEEN THE VISCOSITY COEFFICIENT OF THE RESIDUES AT 50° C. AND THE PERCENTAGE OF LOSS FOR SELECTED TAR SAMPLES.

The values for the hardening index for the weatherometer residues show an increase for the longer periods of exposure, which indicates that some of the hardening has been caused by other factors in addition to evaporation. However, in order to obtain a better indication of what occurs during the different methods of hardening, the viscosity coefficients at 50° C., which are the double logarithms of the kinematic viscosities in centistokes multiplied by 100, were plotted against the percentage of loss for each residue obtained in both the weatherometer and distillation tests. These curves are shown in figure 8. It is seen from the figure that generally the values obtained for the lower amounts of loss in either the weatherometer or distillation test showed good agreement. However, the values for the distillation residues continued on a straight line while for the longer periods of exposure in the weatherometer the viscosity of the residues continued to increase with very little or no additional loss in weight, and thus the curves for the weatherometer data bend upward sharply.

This difference between the values of the viscosity coefficients for the weatherometer data and those for the

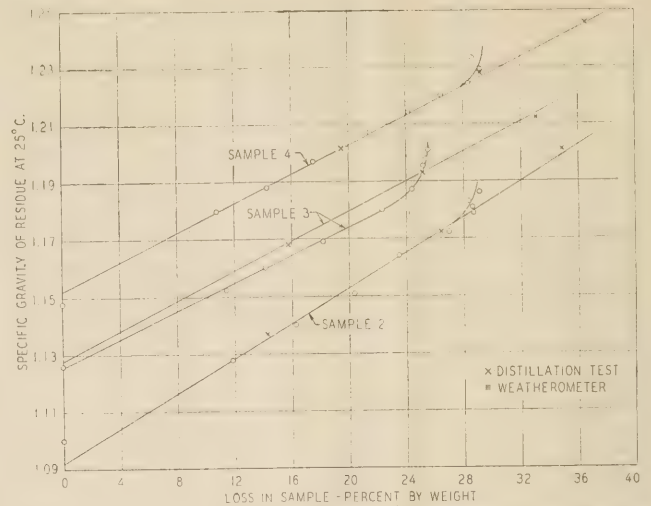


FIGURE 9.—VARIATION OF SPECIFIC GRAVITY WITH PERCENTAGE OF LOSS FOR SPECIAL TAR SAMPLES.

distillation data at equal amounts of loss may be considered a measure of the amount of internal hardening which has taken place. The relative magnitude of this difference is shown on the right-hand side of each graph in figure 8 and it is seen that for these samples the internal hardening is in the order of the amount of sulfonation residue. Sample 2, having high sulfonation indexes, shows about two times as much internal hardening as sample 4, which had very low sulfonation indexes, and sample 3 shows about 1.6 times as much as sample 4.

Figure 9 shows the specific gravities of the various residues plotted against the percentage of loss and the curves show the same trend as do those in figure 8. The points were found to be close to a straight line for the lower amounts of weatherometer loss and for all the distillation points, but the points for the longer periods of exposure showed an increase of specific gravity with very little additional loss. The agreement between the points obtained on the residues from the weatherometer and those obtained on the residues from the distillation test was good for samples 2 and 4, but for sample 3 the points from the distillation were above those for the weatherometer.

The results of the tests on the sand-tar mixes are shown in table 18. The sulfonation indexes and the amount of distillate in the tar up to 300° C. are also repeated here to facilitate comparisons. It is seen that the stability increases very rapidly at first, this increase continuing up to 200 hours and the 400-hour residues show little further increase over the 200-hour specimens. The impact tests proved to be of little value since there was little difference in any of the results, but in each case the value after 400 hours of exposure was equal to or less than the value after 200 hours, which indicates that the samples were becoming more brittle with increased weathering.

It is also interesting to note that the percentage of tar loss from these specimens after 400 hours of weathering was very nearly equal to the percentage of loss in the distillation test up to 300° C. This was not true of the 1/8-inch film exposures of the tar itself. There is no direct relationship between the sulfonation index of either portion of the distillate of the tar binder and the stability of the sand mixes. However, the data shown in table 18 indicate that the stabilities developed in the

(Continued on p. 164)

TRAFFIC GROWTH AND COMPOSITION

1937-1941

BY THE DIVISION OF HIGHWAY TRANSPORT, PUBLIC ROADS ADMINISTRATION

Reported by L. E. PEABODY, Senior Highway Economist

PERMANENTLY installed automatic traffic counters on the rural highways of 47 States were in operation at 657 locations in March 1942. Many of these stations have been operated for 24 hours a day every day since January 1, 1937.¹ They furnish the most complete and accurate data available for the study of traffic characteristics and trends and, from these data, many valuable conclusions may be drawn. Most of these stations are located on State highways; about 10 percent are on local roads.

At many of these points it is possible to separate the total traffic (read from the machines) into its components of passenger cars, various sizes and types of trucks, and busses as a result of manual classifications of traffic made at frequent intervals throughout each of the years and usually taken on weekdays. All of this material has been brought together for analysis.

Traffic on State highways, measured at such stations, increased 19.3 percent from 1939 to 1941, inclusive. Traffic of local passenger cars² increased much more (20.9 percent) than did traffic of foreign passenger cars (14.3 percent). Traffic of trucks and busses upon State highways increased much more (31.9 percent) than did total traffic.

The detailed composition of traffic at all stations where traffic could be separated by type of vehicle is listed in table 1.

TABLE 1.—Composition of traffic on State highways, 1939-1941

Type of vehicle	Percentage of total traffic		
	1939	1940	1941
Passenger cars.....	77.9	77.3	76.1
Light trucks.....	11.8	12.7	12.1
Medium trucks.....	3.8	4.0	4.1
Heavy trucks.....	1.0	.8	1.2
Tractor-truck semitrailer.....	4.2	4.0	5.1
Truck with full trailer.....	.4	.4	.5
Busses.....	.9	.8	.9
Total.....	100.0	100.0	100.0
Number of stations.....	275	292	200

TRAFFIC VOLUME DECLINED SHARPLY IN 1942

The increase in proportion of single-unit trucks was from 16.6 percent in 1939 to 17.4 percent in 1941. Tractor-truck semitrailers increased from 4.2 percent of the total in 1939 to 5.1 percent in 1941. Coupled with the increase in total traffic, this means an increase of 45 percent in the average number per day of tractor-truck semitrailers using the State highways during the period from 1939 to 1941, inclusive.

Figure 1 presents traffic data by months at all stations located on State highways for the period January 1939 to October 1942, inclusive, together with the same data

¹ Applications of Automatic Traffic Recorder Data in Highway Planning, by L. E. Peabody and O. K. Normann. PUBLIC ROADS, January 1941.

² Local vehicles are those carrying license plates of the State in which the station is located.

adjusted for seasonal variation, and the trend of traffic from January 1939, to January 1942, inclusive. Adjustment for seasonal variation includes the following steps: The seasonal variation is determined for the 3 years 1939, 1940, and 1941, with the normal seasonal variation as the weighted average of these data, by months. The adjusted traffic average, presented as a broken line in figure 1, results from dividing the traffic data for each month by the corresponding monthly index of the normal seasonal variation.

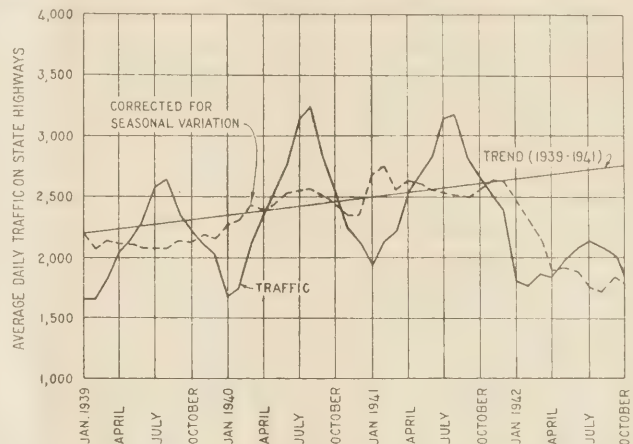


FIGURE 1.—AVERAGE DAILY TRAFFIC BY MONTHS AT AUTOMATIC TRAFFIC RECORDERS ON STATE HIGHWAYS; AVERAGE DAILY TRAFFIC CORRECTED FOR SEASONAL VARIATION; AND TREND OF TRAFFIC (1939-41).

When the adjusted traffic average by months is compared with the monthly trend values, it is found that the ratio varies from a low of 91.1 to a high of 110.4 percent during 1939, 1940, and 1941. In February 1942, the ratio first broke out of this range and dropped to 86.6 percent. For subsequent months in 1942 the ratios have been: March, 81.2; April, 70.2; May, 71.7; June, 69.3; July, 64.1; August, 60.1; September, 65.6; and preliminary data for October, 63.1 percent. Thus traffic volume in the latest month available indicates a decline of 36.9 percent from that normally to be expected. These data furnish a more realistic measure of traffic decline than the simple comparison of traffic volume by months with the volume for the same month a year previous.

One thesis of traffic growth that is sometimes presented maintains that percentage rates of growth are greatest at points of highest traffic volume; i. e., that high rates of growth are associated with large traffic volumes. Figure 2 shows the results of an examination of this thesis. All stations near, or in, defense areas were eliminated from this comparison so that no such possible disturbing element could influence the conclusions. When it is recalled that these data represent traffic counted for 24 hours per day during 365 days per year during 1937 to 1941, inclusive, at points scattered

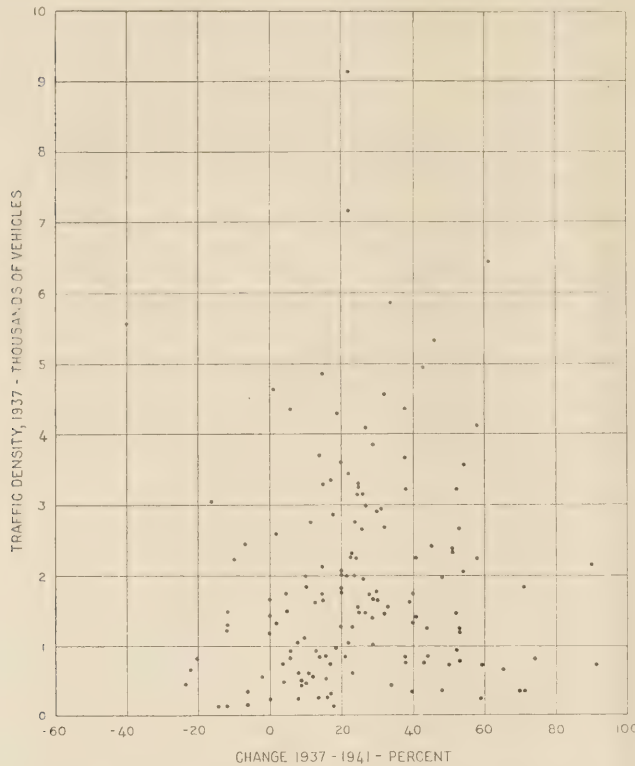


FIGURE 2.—TRAFFIC VOLUME AND PERCENTAGE OF CHANGE IN TRAFFIC VOLUME, 1937-41. (EACH DOT IS ONE STATION.)

all over the United States, the indefensibility of this thesis seems evident. From figure 2, it is seen that at traffic volumes of less than 1,000 vehicles per day, amounts of change vary from an increase of more than 90 percent to a decrease of more than 20 percent. For traffic volumes of from 4,000 to 5,000 per day, the amounts of increase vary from 1 percent to 58 percent.

COMPARISON MADE OF VOLUME CHANGES ON ROUTES CARRYING DIFFERENT TYPES OF TRAFFIC

One hundred and twenty-seven State highway routes could be classified by the State highway departments according to the dominant purposes of the travelers who used them as: Tourist, industrial, farm-to-market traffic, etc. In table 2 a comparison is made of the amount of traffic increase by general type of use during 1937 to 1941, inclusive, and from 1937 to 1940, inclusive. It must be realized that such route classifications according to use are not, and cannot be, truly representative of all the traffic using the route. There will inevitably be some mixture in purpose of use upon all, except possibly a few lightly traveled, routes. These classifications are based upon the purposes of the majority and, in many instances, nearly all of the users.

When the rates of growth in the period from 1937-41 are compared with those in the period 1937-40, some interesting conclusions may be drawn. One is that, at least for this group of 127 routes, the increase in 1941 exceeded the total increase during the three previous years. Another conclusion comes from a comparison of the amounts of increase by purpose of use. When data for 1941 are included the tourist routes show an increase of 38.5 percent as against 21.7 percent for farm-to-market or agricultural routes. If the 1941 traffic is excluded, the increase on farm-to-market routes (15.4

percent) exceeds that upon tourist routes (14.7 percent). In other words, judging from traffic increases upon all routes subject to reasonably accurate classification according to purpose of use, it would seem that tourists took a sizeable "last fling" in 1941. This may be considered together with the far above normal sales of passenger cars in 1941, and with data on the number of automobiles entering national parks during 1941 as compared with those in previous years.

TABLE 2.—Increase in traffic during 1937-41 and 1937-40 according to type of traffic moving over the route

Type of traffic	Number of routes	Average density, 1937	Percent increase	
			1937-41	1937-40
Tourist.....	18	1,953	38.5	14.7
Mines.....	6	1,020	37.7	14.7
Industrial.....	8	2,102	31.3	7.2
Metropolitan.....	12	3,956	28.8	11.6
Tourist and farm-to-market.....	26	2,041	24.6	12.3
Tourist and commercial.....	20	1,701	22.4	12.6
Farm-to-market or agricultural.....	37	1,182	21.7	15.4
Total or average.....	127	1,861	27.5	12.8

Also significant is the fact that routes used mainly by traffic to mines showed almost as great an increase in 1941 as did those used mainly by tourists. However, it should be noted that only six routes to mines were included.

The proportion of traffic carried during various periods of the day has shown almost no change during the years 1937 to 1941 inclusive. Data at 10 stations, with one each in Pennsylvania, Michigan, South Carolina, Florida, Colorado, Washington, and two each in California and Texas, were used to develop this conclusion. The data are presented in table 3.

TABLE 3.—Proportion of total traffic during designated periods for the month of July; data for 1937 to 1941, inclusive

	6 a. m. to 6 p. m.	6 p. m. to 10 p. m.	10 p. m. to 6 a. m.
	Percent	Percent	Percent
1937.....	64.7	21.2	14.1
1938.....	65.4	21.2	13.4
1939.....	65.8	21.3	12.9
1940.....	64.9	21.3	13.8
1941.....	63.9	21.2	14.9

MONTHLY VARIATIONS IN TRAFFIC REMAIN STABLE FROM YEAR TO YEAR

Changes in seasonal variation in traffic have also been small at the automatic traffic recorders during the period from 1939 to 1941, inclusive, as indicated in figure 3.

The seasonal variation is derived by dividing each month's traffic by the traffic in the average month of the year. In this manner the monthly variations in several years may be compared, even though there may be considerable difference in the total traffic of these years. Figure 3 indicates, not that there have been no changes in traffic volume from 1939 to 1941 (actually it is known that traffic increased nearly 20 percent in this period), but that the monthly variations in traffic remained quite stable from year to year.

It is interesting to compare the seasonal variations in motor-vehicle traffic and railway passenger traffic (commutation traffic excluded) during the year 1939. This is presented in figure 4. When it is understood

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DESIGN OF SLAB AND STRINGER HIGHWAY BRIDGES

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A report of an investigation conducted by the University of Illinois Engineering Experiment Station, the Public Roads Administration, and the Illinois Division of Highways

THE slab and stringer bridge is one of the simplest and most conveniently constructed types of highway bridges. Three kinds of such bridges are considered in this paper:

1. The I-beam bridge, which consists of a concrete slab continuous over steel beams, with the beams in the direction of traffic;

2. The composite I-beam bridge, which has shear developers or shear connectors between the beams and the slab which make the structure act as a composite T-beam; and

3. The concrete T-beam bridge, with concrete beams running in the direction of traffic.

The terminology used in describing the component parts of these bridges is illustrated by figures 1 and 2, which are typical views of an I-beam bridge and a concrete T-beam bridge, respectively. The span of the bridge is denoted by a , the spacing of the beams by b , and the thickness of the slab by h . The main reinforcement in the slab is in the direction transverse to the beams, and will be called the transverse reinforcement; the secondary reinforcement in the slab is in the direction of traffic, and will be called the longitudinal reinforcement.

Analyses of slab and stringer bridges are available in Bulletin No. 336 of the University of Illinois Engineering Experiment Station.¹ The bulletin contains coefficients for moments in the beams and the slab for bridges of various proportions. The moment coefficients were determined by analyses taking into account the deflections of the supporting beams. Empirical relations for maximum moments due to standard truck loadings were determined, and are used as a basis for the present studies.

In this paper the comparatively simple formulas which are given for the moments controlling the design of slab and stringer bridges are applicable to a wide range of sizes and proportions of bridges. The procedures described herein are applicable generally to structures with span lengths from 20 to 80 feet, and beam spacings from 5 to 8 feet, for both H-15 and H-20 standard truck loads and truck train loads. The working stresses considered are 18,000 pounds per square inch for both reinforcing and structural steel, and 1,000 pounds per square inch for concrete. The modulus of elasticity of concrete is taken as 3,000,000 pounds per square inch. These values are in accord with the requirements of the current Standard Specifications for Highway Bridges, of the American Association of State Highway Officials, Third Edition, 1941. For other conditions and working stresses, one may derive approximate formulas of the same type as those given herein from the original equations given in Bulletin No. 336.

FUNDAMENTAL RELATIONS OUTLINED

The design of a simple span slab and stringer bridge, after the span and beam spacing have been chosen, is

primarily controlled by the maximum moment in the slab at the center of the panel and by the maximum moment in the beams. The former determines the thickness of the slab and the latter the cross-section of the beams. Both of these moments are dependent on the relative stiffness of the beams and the slab. The relative stiffness, a dimensionless quantity denoted by the symbol H , is defined by the relation

$$H = \frac{E_b I_b}{a EI} \quad (1)$$

where E_b and E are the moduli of elasticity of the materials in the beams and in the slab respectively, in units of lb. per sq. in.,

I_b is the moment of inertia of the cross-section of the beam, in units of in.⁴

I is the moment of inertia per unit of width of the cross-section of the slab in units of in.⁴ per

in. In general, I is taken as $\frac{h^3}{12}$ where h is the thickness of the slab.

a is the span of the bridge, in inches.

The effect of H upon the moments controlling the design is small. This is fortunate, since the magnitude of H is subject to some uncertainty. It is reasonable to use as a modulus of elasticity of the concrete the modulus applying to short time loading, since the major effect of H is on the live load moments. The depth of the slab will have a large influence on the value of H . For the three types of bridges considered in this paper, and for the working stresses used herein, the range in values of H can be summarized reasonably well for designs ordinarily encountered, and the formulas for moments can thereby be made independent of H .

The standard truck loading for which the calculations are made is that specified as the H truck loading in the Standard Specifications for Highway Bridges, previously cited. The standard H truck has the wheels of each axle spaced 6 feet apart, with front and rear axles spaced 14 feet apart. Each of the rear wheels carries a weight which is four-tenths of the total weight of the truck, and each of the front wheels carries a weight of one-tenth the total weight of the truck, or one-fourth the rear wheel weight. The weight of the truck in tons is designated by a numeral following H , as H-20. The rear wheel load P , in terms of which moment coefficients are stated, is the weight on a rear wheel in pounds increased by the impact factor.

Each truck is considered to occupy the central part of a 10-foot traffic lane, and therefore the minimum distance between the center of a wheel and the face of a curb is taken as 2 feet; the minimum distance between centers of wheels of trucks in adjacent lanes is taken as 4 feet. The methods for design given in this paper consider additional trucks in a lane by use of a truck train loading² in which the standard truck may be

¹ The truck train loadings are used herein rather than uniform lane loadings since the former are more representative of actual loadings, and since, in general, the maximum moments in the beams due to lane loadings distributed uniformly are smaller than those due to wheel loads distributed in accordance with the equations given in this paper.

² See notice on p. 166.

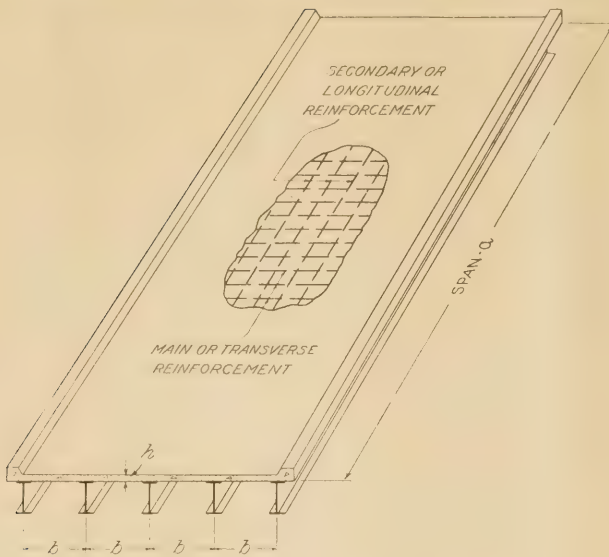


FIGURE 1.—TYPICAL I-BEAM BRIDGE.

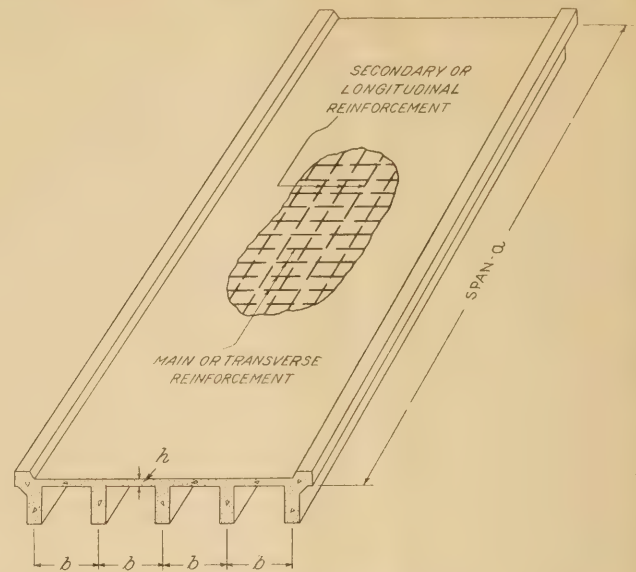


FIGURE 2.—TYPICAL CONCRETE T-BEAM BRIDGE.

followed or preceded at a distance of 30 feet by a similar truck weighing three-fourths as much.

The maximum positive live load moment at the center of a panel of the slab due to standard truck loading is the transverse moment M_t , and is given by equation 12 of Bulletin No. 336, as follows:

$$M_t = P \left[\frac{1.16}{3 + 10 \frac{c}{b}} - 0.040 + 0.024 \frac{a}{10 \text{ feet } \sqrt{H}} + 0.010 \frac{a - 28 \text{ feet}}{10 \text{ feet } \sqrt{H}} \right]$$

In this equation, c is the equivalent diameter of the circular area over which the wheel load is assumed to be distributed, ordinarily taken as 1.25 feet. The quantities a and b are measured in feet and P is measured in pounds. Consequently, the moment will be in units of foot-pounds per foot of width. The last term in the equation takes account of the front wheel loads of the truck, and is to be dropped for spans of less than 28 feet.

The maximum live load moment in a beam, as given by equations 24 and 25 of Bulletin No. 336, is

$$M_b = k \left[\frac{1}{4} Pa + \frac{1}{16} P(a - 28 \text{ feet}) \right]$$

$$k = \frac{b \left(1 - \frac{b}{aH} \right)}{4.40 \text{ feet} + 0.42 \frac{a}{10 \sqrt{H}}}$$

where the last term in the first equation takes account of the front wheel loads and is to be dropped for spans of less than 28 feet. For spans greater than 60 feet, the moment due to an additional truck in each lane may be approximated by the added term

$$k \left[\frac{1}{20} P(a - 60 \text{ feet}) \right]$$

In these expressions, a and b are measured in feet, P is measured in pounds, and the moments in the beam will be in units of foot-pounds.

It is shown in Bulletin No. 336 that the dead load moments in the slab are affected by the method of construction and are subject to considerable uncertainty unless the construction procedure is very carefully controlled. The moment coefficients for dead load given here are intended to apply to average conditions and are generally on the safe side to allow for some of the uncertainties. For I-beam bridges, whether composite action is provided or not, the dead load moment in the slab at centers of panels may be taken as $\frac{1}{8} wb^2$ where w is the magnitude of the dead load per unit of area measured in pounds per square foot. For concrete T-beam bridges, this moment may be taken as $\frac{1}{10} wb^2$ because of the greater stiffness of the concrete T-beams. The live and dead load moments at other points in the slab may be obtained from Bulletin No. 336, but are not necessary for designs made according to the procedures given herein, whereby certain proportions of reinforcement are provided at other points.

The dead load moment in edge or interior beams may be determined from the weight of one panel of the slab, the weight of the beam, and whatever paving allowance is considered. The total dead load moment provided for in all the beams should not be less than the total statical dead load bending moment due to the entire weight of the bridge, including handrails, curbs, sidewalks, and other such details. Similarly, the total live load moment provided for should not be less than the total statical live load bending moment.

COMPOSITE ACTION OBTAINED WITH SHEAR CONNECTORS

Composite action of the slab with steel beams may be considered if adequate provision is made for shear connectors. Such shear connectors may be made up of channels, plates, angles, or other structural elements, welded or riveted to the top flange of the beam, and embedded in the concrete of the slab. To prevent uplift there should be a mechanical anchorage of the connector in the concrete. The load to be carried by the shear connector may be computed by the ordinary formulas of elementary mechanics from the shear on the composite T-beam section.

When the composite structure is constructed in the usual manner, without false work supporting the beams during construction of the slab, the dead load from both

the slab and the beam is carried by the steel beam section alone, but the live load is carried by the composite T-beam section. Where the dead load shear is carried by the steel beam section alone, it should be noted that the shear connector does not have to provide for the dead load action.

The dead load shear varies linearly from the reaction at the end of a beam to zero at the center. It is recommended that the live load shear in a beam be computed from the shear for either truck or truck train loadings by the use of the same proportion, *k*, of a wheel load that is used in determining the moment in the beam. The total force acting on any shear connector may then be computed from the longitudinal shear per unit of length between the beam and the slab, multiplied by the spacing between the shear connectors.

For design purposes, the tentative recommendation is made that the distribution of load over the face of the shear connector be considered linear, from zero at the top of the connector to a maximum at the junction of the connector and the top flange of the beam. The stress in bearing on the concrete may be taken equal to the usual compressive working stress for concrete, and the flexural stress in the shear connector may be taken as the usual working stress for the steel. The spacing of the shear connectors should be not more than 3 to 4 times the depth of the slab. The usual criteria should cover the design of the connection between the shear connector and the beam.

A limited number of tests indicate that when the shear connector is a channel having one flange attached to the beam, the above working stresses may safely be doubled, or the load the shear connector must provide for may be reduced by one-half. Tests of quarter-scale models of I-beam bridges with such shear connectors indicated that the strength of the slab and of the beams may be developed without any evidence of failure of the shear connectors, even with a somewhat less conservative design than that proposed. These recommendations are subject to revision in the light of tests that are now under way.

DESIGN OF SIMPLE SPAN I-BEAM BRIDGES GIVEN

For simple span I-beam bridges, designs of structures with the working stresses considered in the preceding sections indicate values of *H* falling in the range given by the equation:

$$H = (0.4 \text{ to } 0.8) \frac{a}{10 \text{ feet}} \text{-----} (2)$$

where *a* is measured in feet.

This relation applies both for H-15 and H-20 loading, since the difference in slab thickness required for these loadings has the effect of making the values of *H* nearly the same. The effect of considering a paving allowance of 25 pounds per square foot is to give only slightly increased values of *H*.

Under ordinary conditions the slab may be designed for a live load moment *M_l* given by equation 3, which is independent of *H*:

$$M_l = P \left[\frac{1.16}{3 + 10 \frac{c}{b}} + \frac{a}{1000 \text{ feet}} \right] \text{-----} (3)$$

This is the transverse moment at the centers of the panels of the slab (in the direction perpendicular to the beams). The corresponding dead load moment in the slab may be taken as $\frac{1}{8} wb^2$. For a first approximation

it will usually be adequate to assume that the dead load moment is 10 percent of the live load moment.

The moment given by equation 3 will control the amount of transverse reinforcement in the bottom of the slab at the centers of panels. For ordinary designs, the empirical equations given in Bulletin No. 336 indicate that approximately one-fourth as much steel should be used at the top of the slab for transverse reinforcement at the centers of the panels as is used in the bottom. Over the beams the transverse reinforcement at the bottom of the slab should be about one-half, and at the top of the slab about two-thirds to three-fourths, of the transverse bottom steel at the centers of the panels of the slab.

The longitudinal reinforcement required in the slab (in the direction parallel to the beams) may be nearly as much as the transverse reinforcement for short span structures but will be considerably less for long span structures. The following approximation is recommended for the ratio of longitudinal to transverse reinforcement at the bottom of the slab in the central half of the panels:

$$\frac{\text{Longitudinal reinforcement}}{\text{Transverse reinforcement}} = 1 - \frac{a}{200 \text{ feet}} \text{-----} (4)$$

where *a* is measured in feet.

The longitudinal reinforcement in the bottom of the slab over the beams depends on a number of factors, the effects of which are difficult to estimate. However, it seems desirable to provide from one-half to one-third the amount of longitudinal reinforcement that is provided in the central half of the panel, the smaller amount being used for the longer spans.

The live load moment in the beams is given by the following approximate equation,

$$M_b = k \left[\frac{1}{4} Pa + \frac{1}{16} P(a - 28 \text{ feet}) + \frac{1}{20} P(a - 60 \text{ feet}) \right] \text{-----} (5)$$

where the last term is to be dropped for spans of less than 60 feet, and the second term is to be dropped for spans of less than 28 feet. The quantity *k* may be considered as the proportion of a wheel load which effectively contributes to the moment in a beam, and is given by the relation:

$$k = \frac{b}{6 \text{ feet}} \text{-----} (6)$$

where *b* is the beam spacing in feet.

It will be noted that *H* does not enter into these relations, and it has been found that this approximation for the moment in the beams is reasonably accurate for designs falling within the range of proportions considered here.

The dead load moment in the interior beams is determined from the weight of one panel of the slab and the weight of the beam, plus any paving allowance that may be considered. All the beams, edge or interior, should have the same section since the maximum dead plus live load moments in all beams are very nearly the same.

TYPICAL DESIGN COMPUTATIONS GIVEN FOR SIMPLE SPAN COMPOSITE I-BEAM BRIDGE

A composite I-beam bridge will in general offer some economy over a corresponding simple I-beam structure. If composite action is provided for by adequate shear connectors, designs of structures with the working stresses considered here indicate values of *H* generally

about twice as great as for an I-beam bridge of the same span and beam spacing.

Under ordinary conditions the slab may be designed for a live load moment M_l given by the following equation:

$$M_l = P \left[\frac{1.16}{3 + 10 \frac{c}{b}} - 0.025 + \frac{a}{1000 \text{ feet}} \right] \text{-----} (7)$$

The corresponding dead load moment may be taken as $1/8 wb^2$. The transverse reinforcement in the slab may be distributed in the same proportions as for an I-beam bridge not designed for composite action. The relative amount of longitudinal reinforcement at the bottom of the slab in the central half of the various panels may be computed from equation 4. However, over the beams the longitudinal steel in the slab can be considerably less, or may even be omitted entirely.

The live load moment in the beams is given by equation 5 where the quantity k is determined by the relation:

$$k = \frac{b}{5.5 \text{ feet}} \text{-----} (8)$$

The dead load moment in the beams is determined from the weight of one panel of the slab and the weight of the beam, plus any paving allowance that may be considered. Where the beams are not supported during construction of the slab, the dead load moment is carried by the steel beam alone, whereas live load moment is carried by the composite section.

The effective width of the slab, acting as the upper flange of the composite beam, may be taken as b , the spacing of the beams. However, the slab is in addition subjected to local longitudinal flexure in the neighborhood of concentrated loads. This flexure causes essentially a local stress. Furthermore, the longitudinal action of the slab in local flexure is not as significant as the transverse action. Therefore, it is recommended that the compressive stress in the slab, acting as the upper flange of the composite beam, be limited to the usual working stress in concrete, neglecting the local longitudinal flexure. However, in order to provide for extreme cases, it is suggested that the sum of the actual compressive stress due to the action as the upper flange of the beam, plus 50 percent of the stress due to local longitudinal flexure, be limited to an amount one-third greater than the usual working stress for concrete in compression. For this purpose, the ratio of the compressive stress in the slab due to local longitudinal flexure, to the compressive stress due to transverse flexure, may be considered the same as the ratio of longitudinal reinforcement to transverse reinforcement as given in equation 4.

To illustrate the design procedure recommended herein, typical design computations are given in figures 3, 4, and 5. A complete design is given of a composite I-beam bridge of 56-foot 9-inch span, and 6-foot 6-inch beam spacing, corresponding to a 26-foot roadway, for H-15 loading. The calculations are self-explanatory.

In general, a more efficient steel section for composite action would be a beam having a heavier lower flange than upper flange. Such a section may be built up by riveting or welding a cover plate to the lower flange of a rolled beam.

DESIGN OF SIMPLE-SPAN BRIDGES WITH CONCRETE T-BEAM DESCRIBED

In a concrete T-beam bridge the moment of inertia of the supporting beam will usually be very large.

The values of H computed for representative designs are from 4 to 8 times the values given by equation 2. The following rules for design are based on a structure in which all the beams have the same section below the slab.

For usual conditions the slab may be designed for a live load moment M_l given by the following equation:

$$M_l = P \left[\frac{1.16}{3 + 10 \frac{c}{b}} - 0.025 + \frac{a}{2000 \text{ feet}} \right] \text{-----} (9)$$

The corresponding dead load moment in the slab may be taken as $\frac{1}{10} wb^2$.

The moment given by equation 9 will control the amount of transverse reinforcement in the bottom of the slab at centers of panels. For ordinary designs approximately one-fourth as much steel should be used at the top in the transverse direction at the centers of panels of the slab as is used in the bottom. Over the beams the transverse reinforcement at the bottom of the slab should be about one-fourth to one-third, and at the top of the slab about three-fourths to seven-eighths of the transverse steel at the center of the panel, at the bottom of the slab.

The longitudinal reinforcement in the slab (in the direction of the beams) will be considerably less than the transverse reinforcement. The following approximation is recommended for the ratio of longitudinal to transverse reinforcement at the bottom of the slab in the central half of panels:

$$\frac{\text{Longitudinal reinforcement}}{\text{Transverse reinforcement}} = 0.75 - \frac{a}{400 \text{ feet}} \text{---} (10)$$

Over the beams the longitudinal steel may be a purely nominal amount or may even be omitted entirely.

In the concrete T-beam bridge, the T-beam section carries the beam moment for both live and dead loads. The dead load moment in the beams is determined from the weight of one panel of the slab and the weight of the beam. The live load moment is given by equation 5 in which the value of k is as follows:

$$k = \frac{b}{5 \text{ feet}} \text{-----} (11)$$

The compressive stress in the concrete in the longitudinal direction for the T-beam bridge should be subject to the same limitations previously discussed for the composite I-beam bridge, with the exception that the ratio of the compressive stress in the slab due to local longitudinal flexure, to the compressive stress due to transverse flexure, is the same as the ratio of longitudinal reinforcement to the transverse reinforcement as given in equation 10.

For the concrete T-beam structure, the design of stirrups in the beam may be made with the assumptions regarding vertical shear in the beams that were previously discussed in the section concerning design of shear connectors for composite I-beam bridges.

BASES FOR DESIGN OF CONTINUOUS SLAB AND STRINGER BRIDGES AND SKEW BRIDGES GIVEN

No analyses of continuous slab and stringer bridges are available. It is felt, however, that the magnitudes of the maximum moments in continuous bridges may be approximately determined from the relations given above for simple span bridges. The following princi-

SPAN OF BEAMS, $a = 56'-9"$
 BEAM SPACING, $b = 6'-6"$

H-15 TRUCK LOADING
 DIAMETER OF LOADED AREA, $c = 1'-3"$

A.A.S.H.O. SPECIFICATIONS (1941)

$f_s = 18,000$ LB. PER SQ. IN.
 $f_c = 1,000$ LB. PER SQ. IN.
 $n = 10$

	<u>BEAMS</u>	<u>SLAB</u>
WEIGHT ONE REAR WHEEL =	12,000 LB.	12,000 LB.
IMPACT =	<u>3,300</u>	<u>3,600</u>
DESIGN LOAD, $P =$	15,300 LB.	15,600 LB.

DESIGN OF SLAB

FROM EQUATION 7, $M_t = 15600 \left[\frac{1.16}{3 + (10 \times \frac{1.25}{6.5})} - 0.025 + \frac{56.75}{1000} \right] = 4,170$ FT. LB. PER FT.

DEAD LOAD MOMENT FOR $6\frac{3}{4}"$ SLAB = $\frac{1}{8} W b^2 = \frac{1}{8} \times 84.4 \times 6.5^2 = 445$

TOTAL MOMENT = 4,615 FT. LB. PER FT.

REQUIRED EFFECTIVE DEPTH = $5\frac{1}{2}"$
 1" COVER + $\frac{1}{2}$ " BAR DIAMETER = $\frac{1}{4}"$
 TOTAL DEPTH = $6\frac{3}{4}"$

TRANSVERSE BOTTOM STEEL AT CENTERS OF PANELS

$A_s = \frac{4615 \times 12}{18000 \times 0.885 \times 5.5} = 0.632$ SQ. IN. PER FT.

USE: $\frac{1}{2}" \phi$ AT $3\frac{3}{4}"$ C.C.

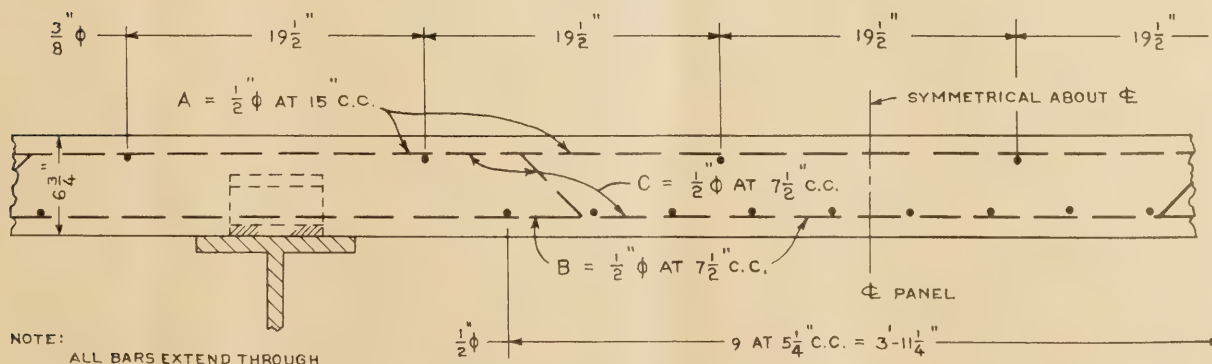
LONGITUDINAL BOTTOM STEEL AT CENTERS OF PANELS

FROM EQUATION 4

$A_s = \left(1 - \frac{56.75}{200} \right) 0.632 = 0.453$ SQ. IN. PER FT.

USE: $\frac{1}{2}" \phi$ AT $5\frac{1}{4}"$ C.C.

REINFORCING BAR LAYOUT



CROSS SECTION OF SLAB

FIGURE 3.—ILLUSTRATIVE DESIGN OF COMPOSITE I-BEAM BRIDGE—DESIGN OF SLAB.

DESIGN OF BEAMS

FROM EQUATION 8 $k = \frac{6.5}{5.5} = 1.182$

FROM EQUATION 5 LIVELOAD $M_o = 1.182 \left[\frac{1}{4} \times 15300 \times 56.75 + \frac{1}{16} \times 15300 (56.75 - 28) \right]$
 $= 289,000 \text{ FT. LB.} = 3,470 \text{ IN. KIPS}$

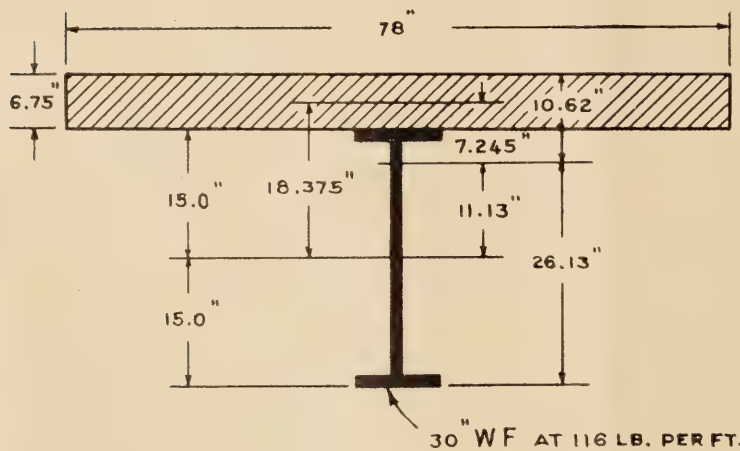
DEAD LOAD: WEIGHT OF SLAB $= 0.0844 \times 6.5 = 0.549 \text{ KIPS PER FT.}$

WEIGHT OF BEAM, (ASSUMED) $= 0.116$

TOTAL DEAD LOAD $= 0.665 \text{ KIPS PER FT.}$

DEAD LOAD MOMENT $= \frac{1}{8} \times 0.665 \times (56.75)^2 \times 12 = 3,215 \text{ IN. KIPS}$

(CARRIED BY I-BEAM ALONE)



A	y	Ay	Ay^2 AND I_o
$\frac{78 \times 6.75}{10} = 52.60$	18.375	966	17,770
34.13	0	0	200
86.73		966	4,919
	$\bar{y} = 11.13$		22,889
	$A\bar{y}^2 =$		-10,770
			$I = 12,119 \text{ IN.}^4$

$\frac{I}{C}$ FOR I-BEAM ALONE $= 327.9 \text{ IN.}^3$

STEEL STRESS

$f_s = \left(\frac{3215}{327.9} + 3470 \times \frac{26.13}{12119} \right) 1000 = 9800 + 7480 = 17,280 \text{ LB. PER SQ. IN.}$

CONCRETE STRESS

$f_c = \left(3470 \times \frac{10.62}{12119} \right) \frac{1000}{10} = 304 \text{ LB. PER SQ. IN.}$

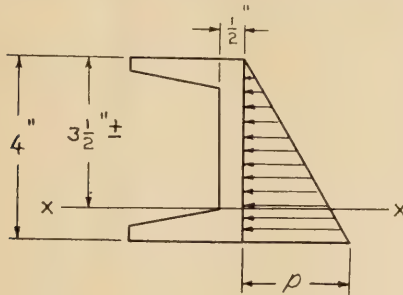
FIGURE 4.—ILLUSTRATIVE DESIGN OF COMPOSITE I-BEAM BRIDGE—DESIGN OF BEAMS.

DESIGN OF SHEAR CONNECTORS

TAKE VERTICAL SHEAR, $V = 24,500$ LB. AT ENDS OF BRIDGE,
 = 15,800 LB. AT QUARTER POINTS,
 = 10,200 LB. AT MIDSPAN.

$$\text{HORIZONTAL SHEAR} = q = \frac{V y A'}{I} = V \times \frac{7.245 \times 52.6}{12119} = 0.0314 V$$

FOR SHEAR CONNECTORS: USE 4" x 13.8 LB. CAR CHANNELS 8" LONG



NOTE THAT ALLOWABLE LOAD ON CONNECTOR COMPUTED FROM USUAL ALLOWABLE STRESSES MAY BE DOUBLED BECAUSE CHANNEL IS USED.

$$\text{ALLOWABLE LOAD} = 2 \left(\frac{1}{2} \times \rho \times 4 \times 8 \right) = 32 \rho$$

IF CONCRETE STRESS GOVERNS: $\rho = f_c = 1,000$ LB. PER SQ. IN.

$$\text{ALLOWABLE LOAD} = 32 \times 1000 = 32,000 \text{ LB.}$$

IF STEEL STRESS GOVERNS:

$$\text{MOMENT ON LINE X-X} = \frac{3.5}{4.0} \rho \times \frac{3.5}{2} \times \frac{3.5}{3} \times 8 = 14.29 \rho$$

$$\frac{I}{C} \text{ OF CHANNEL WEB} = \frac{b d^2}{6} = \frac{8 \times 0.5^2}{6} = 0.333 \text{ IN.}^3$$

$$f_s = 18000 = \frac{m_x C}{I} = \frac{14.29}{0.333} \rho = 42.91 \rho$$

$$\rho = \frac{18000}{42.91} = 419 \text{ LB. PER SQ. IN.}$$

$$\text{ALLOWABLE LOAD} = 32 \times 419 = 13,410 \text{ LB.}$$

∴ STEEL STRESS GOVERNS.

SPACING OF CONNECTORS

AT ENDS :	$q = 0.0314 \times 24,500$	= 770 LB. PER IN.,	$\frac{13,410}{770} = 17.4$ IN. SPACING
AT $\frac{1}{4}$ POINTS :	$q = 0.0314 \times 15,800$	= 496 LB. PER IN.,	$\frac{13,410}{496} = 27.0$ IN. SPACING
AT MIDSPAN :	$q = 0.0314 \times 10,200$	= 320 LB. PER IN.,	$\frac{13,410}{320} = 41.9$ IN. SPACING
MAXIMUM SPACING :	4 X DEPTH OF SLAB	= 4 X 6.75	= 27 IN. SPACING

SHEAR CONNECTOR SPACING DIAGRAM

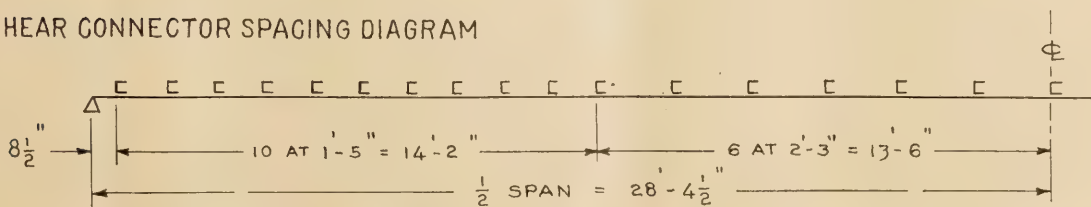


FIGURE 5.—ILLUSTRATIVE DESIGN OF COMPOSITE I-BEAM BRIDGE—DESIGN OF SHEAR CONNECTORS.

ples seem to offer a reasonable basis for the design of a continuous bridge:

1. The slab may be designed as for a simple-span bridge having a span of the beams, *a*, equal to the distance between the "points of inflection" for the particular span of the continuous bridge.

2. The proportion of a single wheel load to be used in determining moments in the beams may be determined from equations 6, 8, or 11, for bridges with steel beams, composite I-beams, or concrete beams, respectively. The moments due to a wheel load should be determined in the usual way for a continuous beam.

3. For I-beam bridges with no composite action pro-

vided for, longitudinal reinforcement for negative moments in the slab should be provided in the region where the beam moments are negative. For composite I-beam bridges or for concrete T-beam bridges the whole slab will be in tension, and may require additional reinforcement accordingly, in the regions of negative beam moments.

No analyses of skew bridges have been made and, in general, the formulas for moments given herein are based only on studies of right bridges. In the absence of other information, however, it is suggested that a skew bridge may be designed as a right bridge having the same length of beams.

(Continued from p. 154)

laboratory tests are more affected by the unsulfonated residue in the portion of the distillate between 300° and 355° C. than by the unsulfonated residue in the dis-

tillate up to 300° C. and generally the mixes made with tars having high sulfonation indexes for the distillate between 300° C. and 355° C. developed lower final stabilities than did those with low sulfonation indexes for this fraction.

TABLE 18.—Results of tests on sand-tar mixes

Sample No.	Time exposed	Sulfonation index		Weight of distillate to 300° C.	Loss of weight of tar		Toughness at 25° C.	Hubbard-Field stability at 25° C.
		Distillate to 300° C.	Distillate from 300° to 355° C.		In 2-inch cylinder	In 1-inch cylinder		
1	0	6.7	2.2	34.6	0	0	80	
	60				24	31	1,550	
	200				32	39	3,750	
	400				35	43	3,840	
2	0	8.9	2.8	33.3	0	0	190	
	60				23	27	1,825	
	200				30	36	3,750	
	400				33	41	4,050	
3	0	3.8	1.4	31.5	0	0	170	
	60				23	28	2,145	
	200				29	35	5,050	
	400				31	39	5,015	
4	0	.7	(1)	34.6	0	0	185	
	60				25	33	4,415	
	200				32	35	8,200	
	400				34	37	8,200	
6	0	4.4	.3	26.5	0	0	165	
	60				21	27	3,345	
	200				25	26	7,000	
	400				28	29	8,000	
7	0	1.6	7	30.2	0	0	175	
	60				22	29	2,210	
	200				27	26	5,400	
	400				29	35	5,450	
8	0	10.4	2.5	29.4	0	0	100	
	60				18	27	1,810	
	200				28	33	3,150	
	400				33	36	4,050	
9	0	9.8	.3	27.9	0	0	150	
	60				22	27	3,850	
	200				29	33	7,650	
	400				31	35	8,350	
10	0	(1)	0	27.9	0	0	225	
	60				19	22	4,730	
	200				25	29	9,000	
	400				26	38	9,700	
11	0	.4	.06	17.5	0	0	580	
	60				11	6	5,250	
	200				17	16	11,400	
	400				18	20	11,700	
12	0	4.9	2.0	31.0	0	0	150	
	60				20	18	1,360	
	200				30	21	4,850	
	400				32	30	4,850	
13	0	3.9	1.6	25.3	0	0	190	
	60				16	21	2,000	
	200				25	25	5,600	
	400				26	26	6,150	
14	0	3.6	.9	33.8	0	0	100	
	60				25	26	1,450	
	200				37	35	5,600	
	400				38	39	5,600	
15	0	3.3	1.4	32.6	0	0	160	
	60				22	25	2,650	
	200				30	26	5,400	
	400				30	28	5,650	

Trace.

This conclusion may seem at variance with the conclusion that those tars having a high sulfonation index hardened more than those with a low sulfonation index. It would seem that the harder residual binders should produce specimens with high stability values, but it is indicated from these stability tests that the inherent bonding strength of the residues from tars with a large amount of unsulfonated residue in the 300° to 355° C. distillation fraction is less than that of tars which have low sulfonation indexes for this fraction.

CONCLUSIONS

This investigation is primarily a study of the sulfonation index test and the effect of the unsulfonated material present in tars on its various properties as shown by laboratory tests. No correlation of this work with the behavior of the tars during construction or under actual service conditions has been made. Consequently, no conclusions can be drawn as to the maximum sulfonation index that is definitely detrimental to the quality of the tar as a road-binding material. It is believed, however, that this investigation justifies the following conclusions:

1. The method of determining the sulfonation index should be modified by decreasing the weight of the sample from 10 to 5 grams and the amount of 37N acid from 30 to 20 milliliters. These modifications increase the proportion of acid to distillate and make possible more vigorous shaking of the sample, which insures more complete sulfonation and more reproducible results.

2. The selective solubility of the distillation fractions in either dimethyl or diethyl sulfate cannot be used as a basis for a quantitative test of the unsulfonated residue to replace the sulfonation index test.

3. There is no direct relationship between the specific gravity of the distillation fraction and the sulfonation index of the tar for that fraction. However, for the tars studied in this investigation and for other tars tested in this laboratory, there are critical values for the specific gravity at 38°/38° C. of the distillate above which the sulfonation index for the particular fraction is less than the maximum requirement usually specified.

4. The critical values for the 0° to 300° C. fraction seem to be about 0.955 at 38°/38° C. for a maximum sulfonation index of 7 and 0.960 at 38°/38° C. for a maximum sulfonation index of 6. For the 300° to 355° C. fraction, the critical values for the specific

gravities at 38°/38° C. were found to be 1.04 for a sulfonation index of 1.5 and 1.05 for a sulfonation index of 1.0.

5. The viscosity coefficient can be used as a basis for comparing the consistency of various materials at a given temperature. The difference in the viscosity coefficient for two residues from the same tar is a measure of the amount of hardening that has occurred.

6. The viscosity coefficient of the residue increases with the amount of loss of distillate, and the average amount of increase for 1 percent of loss is termed "the hardening index." The hardening indexes for the residues from shorter periods of exposure are equal to those for the distillation test but for longer exposures the hardening indexes increase.

7. The difference between the viscosity coefficient of the exposure residue and the viscosity coefficient determined from distillation data for an equal loss is a measure of the internal hardening of the sample. For

the samples tested in this laboratory this is in order of the sulfonation indexes, the sample with the highest indexes having undergone the largest amount of internal hardening.

8. The stability developed by weathered sand-tar mixes is generally in inverse order to the amount of sulfonation residue in the 300° to 355° C. fraction of tar binder.

9. The presence of unsulfonated residue in the tar in considerable percentages has an adverse effect on the binding and weathering properties of the tar.

10. Since the present road tar specifications allow wide variations in the percentage of distillate off at the various cutting temperatures and in the softening point of the distillation residue, nonuniform curing and weathering can be expected from road tars meeting the same specification. For this reason the problem of correlating the amount of unsulfonated residue to the behavior of the tars in service is likely to be difficult.

(Continued from p. 156)

that each series represents country-wide totals, that railway travel of the commutation type (daily home-to-business trips) is excluded, the seasonal changes are very similar except for the "long trip" railway travelers home for the Christmas holidays in December and January, which has no counterpart in highway travel. Of course the highway traffic includes trucks but, as indicated in table 1, approximately 78 percent of it is composed of passenger vehicles.

Early in 1942 it was decided to condense the size of reports of traffic recorder operation issued by the Public Roads Administration in order to produce the information more promptly—in the period of greatest value. As a part of the process of condensation and early release of the material it was decided to present a summary which would include all data received from the States within 3 weeks after the end of the period during which the machines were operated. Thus a summary of traffic data for March would be available on April 21, and so on each month. These preliminary figures would be subject to correction a month later when traffic information from nearly all States had been received; and a complete summary for March would be available on May 21. In table 4 is shown a comparison of the partial and complete data for March, April, and May, 1942. Although data from less than half of the States, and a little more than one-third of the traffic recorders, were available within 3 weeks, the partial or preliminary figures for percentages of change have differed by not more than 1 percent from the complete data received a month later.

TABLE 4.—Comparison of percentage changes in traffic volume as indicated in preliminary and final tabulations, 1942

Month	Summary of preliminary data			Summary of complete data		
	Number of States	Number of stations	Traffic change	Number of States	Number of stations	Traffic change
March...	18	179	Percent -11.5	40	452	-11.3
April...	20	183	-14.8	42	506	-15.8
May....	20	200	-22.6	43	514	-21.7

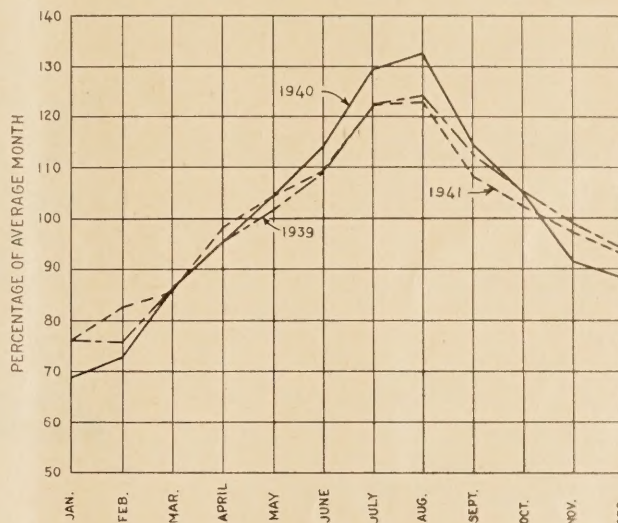


FIGURE 3.—SEASONAL VARIATION IN TRAFFIC RECORDED AT AUTOMATIC TRAFFIC COUNTERS, 1939, 1940, AND 1941.

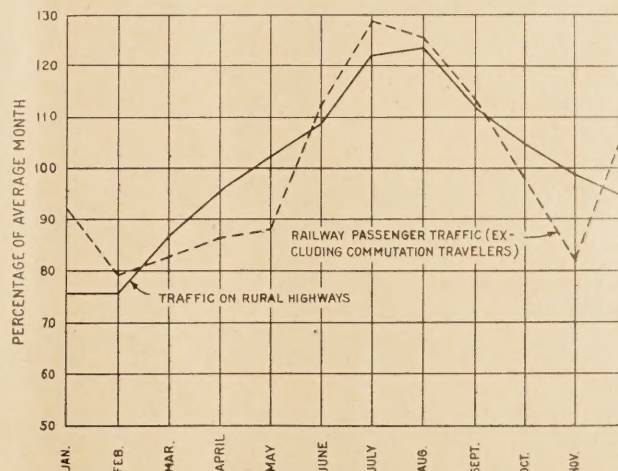


FIGURE 4.—SEASONAL VARIATION IN TRAFFIC ON HIGHWAYS AND RAILWAYS, 1939.

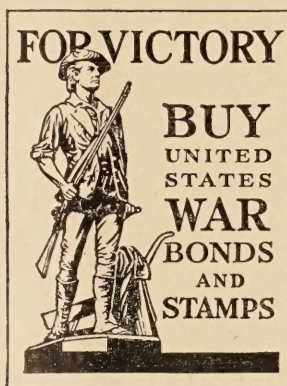
RECENTLY PUBLISHED BULLETINS AVAILABLE

Two bulletins of interest to highway officials have recently been published.

"Moments in I-Beam Bridges" has been issued as Bulletin Series No. 336 of the University of Illinois Engineering Experiment Station. The data reported are based entirely on analytical considerations and give a better understanding of the behavior of the I-beam bridge consisting of a concrete slab continuous over steel beams, a type of structure that has found widespread use for highway bridges. The Public Roads Administration has a limited number of copies of Bulletin No. 336 available for free distribution. Re-

quests should be addressed to the Public Roads Administration, Federal Works Agency, Washington, D. C.

"Stresses in the Corner Region of Concrete Pavements" has been issued as Bulletin No. 157 of the Iowa Engineering Experiment Station. The bulletin reports the results of laboratory stress measurements and field observations, and presents a relatively simple working formula for calculating corner load stresses. Single copies of this 96-page bulletin may be obtained without charge from the Iowa Engineering Experiment Station, Iowa State College, Ames, Iowa.



PUBLICATIONS of the PUBLIC ROADS ADMINISTRATION

Any of the following publications may be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. As his office is not connected with the Agency and as the Agency does not sell publications, please send no remittance to the Federal Works Agency.

ANNUAL REPORTS

- Report of the Chief of the Bureau of Public Roads, 1931. 10 cents.
Report of the Chief of the Bureau of Public Roads, 1932. 5 cents.
Report of the Chief of the Bureau of Public Roads, 1933. 5 cents.
Report of the Chief of the Bureau of Public Roads, 1934. 10 cents.
Report of the Chief of the Bureau of Public Roads, 1935. 5 cents.
Report of the Chief of the Bureau of Public Roads, 1936. 10 cents.
Report of the Chief of the Bureau of Public Roads, 1937. 10 cents.
Report of the Chief of the Bureau of Public Roads, 1938. 10 cents.
Report of the Chief of the Bureau of Public Roads, 1939. 10 cents.
Work of the Public Roads Administration, 1940, 10 cents.
Work of the Public Roads Administration, 1941, 15 cents.

HOUSE DOCUMENT NO. 462

- Part 1 . . . Nonuniformity of State Motor-Vehicle Traffic Laws. 15 cents.
Part 2 . . . Skilled Investigation at the Scene of the Accident Needed to Develop Causes. 10 cents.
Part 3 . . . Inadequacy of State Motor-Vehicle Accident Reporting. 10 cents.
Part 4 . . . Official Inspection of Vehicles. 10 cents.
Part 5 . . . Case Histories of Fatal Highway Accidents. 10 cents.
Part 6 . . . The Accident-Prone Driver. 10 cents.

MISCELLANEOUS PUBLICATIONS

- No. 76MP . . . The Results of Physical Tests of Road-Building Rock. 25 cents.
No. 191MP . . . Roadside Improvement. 10 cents.
No. 272MP . . . Construction of Private Driveways. 10 cents.
No. 279MP . . . Bibliography on Highway Lighting. 5 cents.
Highway Accidents. 10 cents.
The Taxation of Motor Vehicles in 1932. 35 cents.
Guides to Traffic Safety. 10 cents.
An Economic and Statistical Analysis of Highway-Construction Expenditures. 15 cents.
Highway Bond Calculations. 10 cents.
Transition Curves for Highways. 60 cents.
Highways of History. 25 cents.
Specifications for Construction of Roads and Bridges in National Forests and National Parks. 1 dollar.

DEPARTMENT BULLETINS

- No. 1279D . . . Rural Highway Mileage, Income, and Expenditures, 1921 and 1922. 15 cents.
No. 1486D . . . Highway Bridge Location. 15 cents.

TECHNICAL BULLETINS

- No. 55T . . . Highway Bridge Surveys. 20 cents.
No. 265T . . . Electrical Equipment on Movable Bridges. 35 cents.

Single copies of the following publications may be obtained from the Public Roads Administration upon request. They cannot be purchased from the Superintendent of Documents.

MISCELLANEOUS PUBLICATIONS

- No. 296MP . . . Bibliography on Highway Safety.
House Document No. 272 . . . Toll Roads and Free Roads.
Indexes to PUBLIC ROADS, volumes 6, 7, 11, 12, 15, and 17-22, inclusive.

SEPARATE REPRINT FROM THE YEARBOOK

- No. 1036Y . . . Road Work on Farm Outlets Needs Skill and Right Equipment.

REPORTS IN COOPERATION WITH UNIVERSITY OF ILLINOIS

- No. 303. . . Solutions for Certain Rectangular Slabs Continuous Over Flexible Support.
No. 304. . . A Distribution Procedure for the Analysis of Slabs Continuous Over Flexible Beams.
No. 313. . . Tests of Plaster-Model Slabs Subjected to Concentrated Loads.
No. 314. . . Tests of Reinforced Concrete Slabs Subjected to Concentrated Loads.
No. 315. . . Moments in Simple Span Bridge Slabs With Stiffened Edges.
No. 336. . . Moments in I-Beam Bridges.

UNIFORM VEHICLE CODE

- Act I.—Uniform Motor Vehicle Administration, Registration, Certificate of Title, and Antitheft Act.
Act II.—Uniform Motor Vehicle Operators' and Chauffeurs' License Act.
Act III.—Uniform Motor Vehicle Civil Liability Act.
Act IV.—Uniform Motor Vehicle Safety Responsibility Act.
Act V.—Uniform Act Regulating Traffic on Highways.
Model Traffic Ordinances.

A complete list of the publications of the Public Roads Administration, classified according to subject and including the more important articles in PUBLIC ROADS, may be obtained upon request addressed to Public Roads Administration, North Interior Bldg., Washington, D. C.
