

# Plasticized Sulfur Compositions for Traffic Marking

C. KINNEY HANCOCK

*Texas Engineering Experiment Station,  
Texas A. & M. College System, College Station, Tex.*

**T**HE marked increase in motor traffic since 1900 has resulted in ever-increasing demands for suitable materials for highway and street traffic markings to promote safer driving. The magnitude of this problem, in terms of cost of materials and of labor, is not generally appreciated. For example, the highway motorist who relies so much on the center line traffic stripe of a two-lane highway knows little about the cost and effort required for its installation and maintenance. According to a practical formula used by highway paint engineers, the number of gallons of paint required per mile for a continuous 4-inch traffic stripe is approximately equal to the thickness of the applied paint film in mils.

Much research has been, and remains to be, carried out on traffic marking materials. The principal factors of interest are: color and color retention, both day and night visibility, resistance to weathering and traffic abrasion, and quick drying without accompanying difficulties in application. The literature concerning these factors is abundant; a compact treatment may be found in ten articles and an annotated bibliography of the Highway Research Board (7).

For several years, the Texas Engineering Experiment Station has conducted studies of traffic marking materials. Keese and Benson (8, 9) have reported successful results of one of these studies which led to the development of a very serviceable hot-melt rosin-alkyd resin striping composition. The present article is concerned with another aspect of this research.

The study reported herein was concentrated on the development of a more suitable yellow striping material to be used as a dash stripe next to and parallel to the highway center stripe to indicate no-passing zones in areas where visibility ahead is insufficient for safe passing. This method for marking no-passing zones is the practice of the Texas Highway Department.

For many years, the Texas Highway Department and others have used a very serviceable white center line stripe which is laid by first striping the pavement with hot asphalt and then applying a layer of small, crushed limestone aggregate, most of which is cemented in place as the asphalt cools. Surface traffic abrasion of the relatively soft limestone serves to restore the white color and offset traffic soiling. Moreover, the slight elevation of this stripe above the pavement is of some value to the motorist, in that it "tells" him when he has unintentionally passed over the stripe. For the present study, the success of this white stripe directed interest toward the development of a similar stripe using yellow aggregate. It was found that limestone aggregate could be stained by impregnating the aggregate with an ammoniacal solution of an ammonia-soluble, water-insoluble yellow pigment (such as zinc chromate), draining, and then allowing the ammonia to evaporate. On crushing the dried, stained aggregate, it was found that the staining did not extend far below the surface. As a result, further study along this line was abandoned, as integral staining was needed in order to achieve the color-restoring feature resulting from traffic abrasion. The above-described method of staining aggregate is a simpler variation of that of Koebig (11), in which the aggregate is impregnated with a mixture of ammonia and solutions of two salts which will form, by metathesis, the water-insoluble, ammonia-soluble pigment.

It is believed that Koebig's procedure is of questionable value since, on subsequent drying, it would lead to the simultaneous deposition of water-soluble matter along with the water-insoluble pigment and this would result later in disintegration of the pigment by leaching action of rain.

As a source of yellow aggregate, crushed, integrally colored concrete appeared to be of some interest. Mortar briquets were made using yellow pigment and white portland cement along with either sand or small limestone chips. After curing, the briquets were crushed and tested for color retention and for resistance to loss by abrasion. Satisfactory color retention was found for several commercially available yellow cement colors, and the crushed aggregate from colored briquets showed resistance to loss by abrasion equal to or greater than that for crushed aggregate from uncolored control briquets. However, as the crushed, yellow aggregate showed much greater loss by abrasion than did crushed limestone aggregate, no more studies were made along this line.

Sulfur appeared to be a promising material for yellow traffic markings because of its low cost, stability, yellow color, and short setting-up time. The natural color is not sufficiently intense for traffic marking, but is helpful in that less additional yellow pigment would be required to obtain the desired color. In spite of its low cost, sulfur has been in short supply until recently, when the situation eased up considerably.

The results of preliminary traffic marking tests with molten sulfur alone were not encouraging because, after solidifying, the sulfur was not bonded satisfactorily to the pavement and moreover was brittle and underwent early and extensive loss by traffic abrasion. If the sulfur was overheated during the melting operation, the resulting viscous product was dark in color and showed no better service performance as a traffic marking material than that discussed above. In this connection, the viscosity-temperature behavior of liquid sulfur, as found by Bacon and Fanelli (1), is of interest. At the melting point (119° C.) liquid sulfur has a viscosity of about 11 centipoises. With rising temperature, the viscosity slowly falls to about 9 centipoises at about 158° C., then rises rapidly to about 93,200 centipoises at about 187° C., and thereafter falls rapidly.

## SULFUR PLASTICIZERS

In view of the unsuccessful results obtained with molten sulfur alone, it appeared necessary to plasticize the sulfur by adding a suitable material. The following materials have been tested as plasticizers of sulfur: Thiokol Type A (polyethylene tetrasulfide), Thiokol Type A plus wood rosin, *tert*-butyl polysulfides (14), Aroclor (chlorinated diphenyl), Halowax (chlorinated naphthalene), wood rosin, natural rubber, Butyl rubber, olive oil, dibutyl phthalate, *p*-dichlorobenzene, and alkyd resin (No. 31 Solid Beckosol, Reichhold Chemicals, Inc.).

In most cases, the results of small scale laboratory tests were sufficient for tentative evaluation of the material as a plasticizer of sulfur. These tests involved melting the mixture, thoroughly agitating, making a smear on a concrete test block, and then observing the time-cooling behavior of the mixture while stirring after heating was discontinued. A powdery or brittle smear with

no appreciable lowering of the solidifying point of the sulfur was considered sufficient to discard the material. In some cases, it was visually apparent that the sulfur and additive were incompatible. In more promising cases, larger batches of molten mixture were prepared and test traffic stripes laid in order to observe performance under traffic loads.

The first three of the above-listed materials showed the best plasticizing action on sulfur. Initial results with sulfur plasticized with *tert*-butyl polysulfides showed great promise, but this indication was short-lived, for test traffic stripes laid with such compositions failed rapidly after rains, owing to water solubility of the plasticizer. Succeeding studies were largely concentrated on the use of Thiokol Type A as a plasticizer. Recently, some very promising results have been obtained by using Thiokol Type A with wood rosin for plasticizing sulfur.

Credit for the use of Thiokol as a sulfur plasticizer is due Rueckel and Duecker (13), who used a mixture of 60 parts of sulfur, 10 parts of Thiokol, and 30 parts of aggregate as a jointing material for clay products.

#### YELLOW PIGMENTS FOR PLASTICIZED SULFUR

Very good results were obtained with two pigments of the Hansa Yellow type: Reichhold's 1550 Hansa Yellow (the coupling product between diazotized *p*-nitroaniline and acetoacetanilide) and Du Pont's Toluidine Yellow YT-445-D (the coupling product between diazotized *m*-nitro-*p*-toluidine and acetoacetanilide). Contrary to expectations, cadmium sulfide was unsatisfactory. The yellow inorganic chromate pigments were of speculative interest, but they were not tried because of skepticism concerning the advisability of heating a mixture of sulfur, organic plasticizer, and a metallic chromate. Moreover, technical personnel of the Texas Gulf Sulphur Co. (9) questioned the advisability of using chromates for the purpose.

Kobbe (10) claims that certain aromatic diamines are miscible with and react with sulfur at about 200° C. to form a yellow color. This method for coloring sulfur was not tried in the present study because it was not considered advisable to heat the sulfur above about 155° C.

#### BACTERICIDES AND OTHER ADDITIVES

Previously reported evidence indicates that traffic stripes laid with plasticized sulfur compositions might undergo bacterial attack that would result in deterioration and loss of bond to the pavement. Beekwith and Bovard (2) attributed breakdown of pipeline joints to bacterial attack upon the sulfur-containing sealing compound. Duecker and associates (4) and Frederick and Starkey (6) found that sulfur sealing compounds were attacked by the sulfur bacterium *Thiobacillus thiooxidans*. Both groups of these investigators found that bacterial attack could be retarded or prevented by the use of suitable bactericides. Duecker and associates concluded that the use of water-soluble salts, as bactericides, in sulfur cements is deleterious. Of a large number of bactericides tested, Frederick and Starkey found Monsanto's Santobrite (sodium pentachlorophenate) most effective.

In this study, Monsanto's Santophen 1 (*o*-benzyl-*p*-chlorophenol) and Dow's Dovicide 7 (pentachlorophenol) were tested. Results indicate that the presence of a small amount of either of these bactericides is beneficial.

Serviceable plastic compositions resulted when powdered silica and Ottawa sand (20- to 30-mesh) were tested as fillers for plasticized sulfur. In many tests, glass beads (largely 20- to 50-mesh) have been used in plasticized sulfur compositions to improve night visibility of the resulting traffic stripe. The use of both glass beads and Ottawa sand in traffic stripes resulted in greater impairment of color as the result of accumulation of foreign matter on the rough surface.

#### EXPERIMENTAL PROCEDURE

Usually, 600- to 1200-gram (not including glass beads or filler) batches of plasticized sulfur were prepared, using 1-quart motor oil cans for containers. Larger batches were prepared in 46-ounce cans. For convenience on the small scale, crude sulfur (99.5 to 99.9% sulfur) was crushed to pass a No. 10 sieve. The sulfur was mixed thoroughly with the pigment on a flat surface and the mixture transferred to the can and placed in a 2-quart mineral oil bath. A desiccator plate in the bottom of the bath supported the can and prevented local overheating of the sulfur. The mixture was melted and mixed without allowing the oil bath temperature to exceed 160° C., this maximum bath temperature applying throughout the remainder of the procedure. The plasticizer was added in small portions with good stirring. When Thiokol Type A was used, in spite of slow addition with stirring, the majority of this plasticizer balled up and did not begin to disperse into the sulfur until stirring had been prolonged; thereafter, the Thiokol dispersed rapidly to give a viscous mixture, depending on the percentage, which finally became more mobile after further stirring and heating. Considerable frothing always occurred during the addition of Thiokol to the molten sulfur. Technical personnel of the Thiokol Chemical Corp. (15) attribute this frothing to entrapped air in the Thiokol, which is in agreement with observations made in this study.

Other additives, if used, were incorporated into the molten mixture and the material taken from the laboratory to the test area (streets on the campus of the A. and M. College of Texas). A portable gasoline camp stove was used to keep the mixture hot until used. The pavement was swept and a 4-inch transverse stripe was laid from the center line of the street toward the curb, using a wooden screed box (inside dimensions: 4 inches wide, 5 inches long, 4 inches deep) with a steel gate which could be raised or lowered to control the film thickness.

The excess of plastic material in the can was kept for comparison in observing the color retention of the test stripe. After laying, the test stripes were observed at various times for resistance to traffic abrasion and for color retention. As reported in the tables, per cent loss indicates the percentage of exposed pavement within the area which was originally covered by the stripe. In most cases where beads had been used in the plastic mixture, additional beads were sprinkled on the hot test stripe immediately after laying.

About 1100 vehicles passed over these test stripes daily. The approximate traffic classification was: 90% passenger cars, 7% trucks, and 3% busses.

#### RESULTS

In addition to very extensive small-scale laboratory tests, 99 traffic test stripes were laid during this investigation. The service performance of the majority of these stripes led to the rejection or further study of certain materials or of processing conditions; the conclusions reached have been discussed semiquantitatively above. Data for certain other representative traffic test stripes are presented below.

In a series of experiments, mixtures of 855 grams of crude sulfur, 45 grams of Thiokol Type A, 3 grams of bactericide (except as noted), and 200 grams of beads (except as noted) at about 130° C. were used to lay 4-inch transverse traffic stripes with a film thickness of 0.5 mm. Except as noted, beads were sprinkled onto the stripes immediately after laying. In all cases, the stripes had set up and were ready to receive traffic within 5 minutes after laying. No pigment was used in any of the stripes and they all showed a fair light olive-yellow color.

The variable factors and results of observations of loss by traffic abrasion and weathering are shown in Table I.

The results of the 45- and 67-week observations are misleading and are unfair as concerns the merits of the test stripes. Some time prior to the 45-week observation, construction was begun on a new boulevard which was designed to intersect the test stripe area. During this construction, the test stripes were subjected to abnormal wear from heavy construction equipment and this contributed an undetermined amount to the large losses observed after 45 and 67 weeks.

These eight stripes suffered considerable traffic discoloration

TABLE I. PERFORMANCE OF TRAFFIC STRIPES WITHOUT PIGMENT

| No. of Test      | Bactericide | Loss after Weeks Indicated, % |     |    |                 |                 |
|------------------|-------------|-------------------------------|-----|----|-----------------|-----------------|
|                  |             | 16                            | 29  | 34 | 45 <sup>a</sup> | 67 <sup>a</sup> |
| 148 <sup>b</sup> | None        | 15                            | 80  | 85 | ..              | ..              |
| 149 <sup>b</sup> | Dowicide 7  | 25                            | 80  | 85 | ..              | ..              |
| 150 <sup>b</sup> | Santophen 1 | 25                            | 80  | 90 | ..              | ..              |
| 157              | Santophen 1 | 1                             | 10  | 10 | 32              | 80              |
| 158              | Dowicide 7  | 0.5                           | 10  | 20 | 35              | 67              |
| 159              | None        | 0.5                           | 20  | 32 | 55              | 75              |
| 160 <sup>c</sup> | Dowicide 7  | 0                             | 0.5 | 3  | 15              | 85              |
| 161 <sup>c</sup> | None        | 2                             | 20  | 30 | 40              | 95              |

<sup>a</sup> See discussion.<sup>b</sup> No beads used.<sup>c</sup> Laid on asphalt pavement, other stripes laid on concrete pavement.

TABLE II. PERFORMANCE OF TRAFFIC STRIPES WITH PIGMENT

| No. of Test        | Type of Pavement | Bactericide | Loss after Weeks Indicated, % |    |    |    |    |    |    |                 |                 |                 |
|--------------------|------------------|-------------|-------------------------------|----|----|----|----|----|----|-----------------|-----------------|-----------------|
|                    |                  |             | 8                             | 12 | 16 | 20 | 29 | 34 | 39 | 45 <sup>a</sup> | 49 <sup>a</sup> | 67 <sup>a</sup> |
| 119 <sup>b,c</sup> | Asphalt          | None        | ..                            | 5  | .. | 25 | .. | 50 | 70 | ..              | 75              | ..              |
| 120 <sup>b,c</sup> | Concrete         | None        | 5                             | .. | .. | 67 | .. | 70 | 73 | ..              | 87              | ..              |
| 152 <sup>d</sup>   | Asphalt          | Santophen 1 | ..                            | .. | 0  | .. | 10 | 12 | .. | 20              | ..              | 30              |
| 153 <sup>d</sup>   | Concrete         | Santophen 1 | ..                            | .. | 0  | .. | 4  | 5  | .. | 25              | ..              | 45              |
| 155 <sup>d</sup>   | Asphalt          | Dowicide 7  | ..                            | .. | 0  | .. | 20 | 22 | .. | 25              | ..              | 35              |
| 156 <sup>d</sup>   | Concrete         | Dowicide 7  | ..                            | .. | 0  | .. | 2  | 5  | .. | 25              | ..              | 60              |

<sup>a</sup> See discussion in connection with Table I.<sup>b</sup> No beads added to plastic mixture before laying.<sup>c</sup> Toluidine Yellow YT-445-D used.<sup>d</sup> 1550 Hansa Yellow used.

during the first few days after laying, but thereafter the color progressively improved from weathering and traffic abrasion until it was as good as (in some cases, better than) the original color. The results of the first three tests strongly indicate that glass beads increase service performance in addition to improving night visibility. From the results of tests 159 and 161, it appears that the addition of bactericide is beneficial, but there is insufficient evidence from other tests to warrant a comparison of the effectiveness of the two bactericides used.

In another series of tests, mixtures of 792 grams of crude sulfur, 90 grams of Thiokol Type A, 18 grams of pigment, 3 grams of bactericide (except as noted), and 200 grams of beads (except as noted) at about 130° C. were used to lay 4-inch transverse traffic stripes with a film thickness of 0.5 mm. In all cases, beads were sprinkled onto the stripes immediately after laying. All of the stripes had set up and were ready to receive traffic within 5 to 10 minutes after laying, and all showed a good olive-yellow color.

The variable factors and results of observations of loss by traffic abrasion and weathering are shown in Table II.

It is apparent from Table II that stripes represented by tests 119 and 120 were inferior to the other four. Evidence from other experiments has shown that Toluidine Yellow-YT-445-D and 1550 Hansa Yellow have about the same merits as pigments for plasticized sulfur, so the early failure of these two stripes cannot be attributed to the use of a different pigment. In view of the results shown in Table I, it is concluded that the poor performance of these two stripes was due to the absence of both bactericide and beads in the plastic mixture. The results shown in the last four lines of Table II indicate slightly better performance on concrete pavement than on asphalt pavement. All six of the stripes underwent early traffic discoloration, but the color soon recovered and held up fairly well thereafter. Perhaps, the early traffic discoloration (nearly always noted) might be corrected by using a surface drier—e.g., a cobalt drier; however, Keese (8) made such studies with hot-melt rosin-alkyd resin striping compositions and obtained results which were largely inconclusive.

These six plastic compositions containing 10% of Thiokol Type A (excluding the beads) striped well with the screed box and did not spread after laying. On the other hand, considerable spreading after laying occurred with the compositions containing 5% of Thiokol Type A (see Table I). At the same time, however, the setting-up time required before opening to traffic increased

with increasing content of Thiokol. From over-all summer results of this project, it has been noted, as a very rough approximation, that the setting-up time in minutes is about equal to the percentage of Thiokol in the plastic mixture.

The results of test stripes laid with compositions containing some other plasticizers are shown in Table III. The stripes were laid with 600-gram portions of molten mixture at about 130° C. The gate opening on the screed box was 0.5 mm., but spreading occurred after laying in most cases. All of the stripes set up in less than 3 minutes and showed a fairly good lemon-yellow or light olive-yellow color. No pigment, bactericide, or beads were used in these stripes.

The results shown in Table III indicate that the Aroclors and Halowaxes, in the concentrations and under the conditions used, do not have sufficient plasticizing action on sulfur. The results of tests 130, 128, 142, and 131 show no significant difference in performance of the compositions on asphalt pavement as compared to that on concrete pavement.

The results of some recent tests with compositions containing small amounts of wood rosin show considerable promise. It will be necessary to observe the test stripes for a much longer period before a true evaluation can be made, but the results to date are of interest.

Using a mixture of 1200 grams of plasticized material plus 300 grams of beads, 4-inch transverse stripes with a film thickness of 1 mm. were laid at 140° C. on concrete pavement. Additional beads were sprinkled heavily on the stripes immediately after laying. All of the stripes were set up and ready to receive traffic within 15 minutes after laying.

The variable conditions of laying and the results of observations to date are shown in Table IV.

All these test stripes showed a good yellow at first, and underwent early traffic discoloration, but gradually the color returned more or less to the original. These stripes show fairly good light reflectance from the beading. From the results to date, it ap-

TABLE III. TESTS WITH OTHER PLASTICIZERS

| No. of Test      | Composition, % |           |                   | Loss after Weeks Indicated, % |    |    |    |    |
|------------------|----------------|-----------|-------------------|-------------------------------|----|----|----|----|
|                  | Crude sulfur   | Thiokol A | Other plasticizer | 5                             | 9  | 17 | 30 | 36 |
| 140              | 95             | 0         | Aroclor 1254      | 2                             | .. | 90 | 93 | 95 |
| 141              | 95             | 0         | Aroclor 1260      | 12                            | .. | 90 | 65 | 92 |
| 130              | 95             | 0         | Aroclor 5460      | ..                            | 10 | 67 | 80 | 90 |
| 128 <sup>a</sup> | 95             | 0         | Aroclor 5460      | ..                            | 10 | 75 | 92 | 97 |
| 142              | 95             | 0         | Halowax 1000      | 1                             | .. | 40 | 50 | 88 |
| 131              | 95             | 0         | Halowax 1001      | ..                            | 10 | 50 | 60 | 80 |
| 132 <sup>a</sup> | 95             | 0         | Halowax 1001      | ..                            | 10 | 33 | 50 | 85 |
| 138              | 90             | 0         | Aroclor 5460      | 10                            | .. | 80 | 85 | 95 |
| 146              | 90             | 5         | Aroclor 1254      | ..                            | 0  | 1  | 50 | 65 |
| 147              | 90             | 5         | Aroclor 1260      | ..                            | 0  | 0  | 40 | 50 |
| 143              | 90             | 5         | Aroclor 5460      | 0                             | .. | 45 | 50 | 52 |
| 145              | 90             | 5         | Halowax 1000      | 0                             | .. | 5  | 50 | 50 |
| 144              | 90             | 5         | Halowax 1001      | 0                             | .. | 10 | 40 | 50 |

<sup>a</sup> Laid on asphalt pavement, other stripes laid on concrete.

TABLE IV. RESULTS WITH SULFUR-THIOL TYPE A-WOOD ROSIN MIXTURES

| No. of Test      | Composition of Plastic Mixture, % |           |                |                  |            | Loss after Weeks Indicated, % |    |    |    |    |    |    |    |    |  |
|------------------|-----------------------------------|-----------|----------------|------------------|------------|-------------------------------|----|----|----|----|----|----|----|----|--|
|                  | Crude sulfur                      | Thiokol A | Pigment        | Bactericide      | Wood rosin | 8                             | 11 | 14 | 16 | 21 | 26 | 30 | 36 | 41 |  |
|                  |                                   |           |                |                  |            |                               |    |    |    |    |    |    |    |    |  |
| 172 <sup>a</sup> | 82.5                              | 12        | 5 <sup>b</sup> | 0.5 <sup>c</sup> | 0          | 42                            | 55 | 70 | 85 | 85 | 87 | 88 | 93 | 98 |  |
| 176 <sup>a</sup> | 76                                | 15        | 5 <sup>b</sup> | 0.5 <sup>c</sup> | 3.5        | 0                             | 0  | 0  | 0  | 0  | 0  | 1  | 2  | 4  |  |
| 178 <sup>a</sup> | 84.5                              | 10        | 3 <sup>b</sup> | 0.5 <sup>d</sup> | 2          | 0                             | 0  | 0  | 1  | 2  | 5  | 6  | 13 | 24 |  |
| 179 <sup>a</sup> | 82.5                              | 12        | 3 <sup>e</sup> | 0.5 <sup>d</sup> | 2          | 0                             | 0  | 8  | 15 | 20 | 30 | 36 | 43 | 50 |  |
| 180 <sup>f</sup> | 82.5                              | 12        | 3 <sup>e</sup> | 0.5 <sup>d</sup> | 2          | 0                             | 0  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |  |
| 181 <sup>g</sup> | 82.5                              | 12        | 3 <sup>e</sup> | 0.5 <sup>d</sup> | 2          | 0                             | 0  | 0  | 0  | 0  | 0  | 0  | 3  | 10 |  |

<sup>a</sup> Pavement swept only.<sup>b</sup> 1550 Hansa Yellow.<sup>c</sup> Dowicide 7.<sup>d</sup> Santophen 1.<sup>e</sup> Toluidine Yellow YT-445-D.<sup>f</sup> Swept, scrubbed, and dried with blowtorch.<sup>g</sup> Swept, scrubbed, and air dried.

pears that the incorporation of a small amount of wood rosin is beneficial. The film thickness was greater and the laying temperature higher than in previously reported tests.

The results of tests 179, 180, and 181 are of interest because the only difference in these three tests was in the pretreatment of the pavement. The late partial failure of stripe 181 may be largely attributed to faulty laying which resulted from fouling of the screed box. From these results, it appears that the pavement should be washed before the stripe is laid, but this indication is inconclusive in view of the results of tests 176 and 178 and earlier tests.

**PAINT STRIPE CONTROLS.** No traffic test stripes, using conventional traffic paints, were laid in this project, but this was unnecessary, as Keese (8), working on a parallel project, laid several representative traffic paint test stripes in the same test area and at the same time. A chlorinated rubber traffic paint test stripe had an effective life of 7 months, while a stripe laid with Pliolite traffic paint gave about 10 months of effective service. Several other traffic paint test stripes had to be repainted several times during 8 to 10 months of testing. It is evident from Table IV that some of the plasticized sulfur test stripes have given 10 months or more of effective service.

#### DISCUSSION

The studies reported in this article were conducted on a small laboratory-field scale. Studies of larger scale apparatus were not made because Keese (8) had already developed a simple, serviceable machine for the purpose and also because of the assurance by highway engineers that the required apparatus would be provided if plasticized sulfur proved to be useful for traffic marking.

Certainly, uniform heating will be a problem in preparing and laying molten sulfur compositions. As direct heating is apparently not feasible, an oil-jacketed kettle will probably be required to prevent local overheating. Because of this heating problem, some early studies were made with carbon disulfide solutions of sulfur. Such solutions were used to paint stripes on pavement, but the resulting film was excessively thin even after several applications of the solution and extensive loss from traffic abrasion and weathering occurred almost immediately. In an effort to improve such solutions for traffic marking, unsuccessful attempts were made to incorporate wood rosin in carbon disulfide solutions of sulfur.

It is believed that the development of a cold-mix plastic sulfur composition deserves further investigation. Recently, Massa, Colon, and Schurig (12) reported on the results of an extensive study of Thiokol polymers dispersed in solvents containing other resins as protective coatings for steel. An appropriate adaptation of their technique might lead to a successful method for cold-mixing plastic sulfur compositions. Unsuccessful tests were made of sulfur-Thiokol Type A compositions as coating materials for steel. However, no primers were used in any of the tests, though Massa and associates found that primers were required for coating steel.

Duecker and Schofield (5), in discussing the use of plasticized sulfur (60% sulfur, 10% olefin polysulfide, and 30% aggregate) as a jointing material for clay products, reported that the applied composition emitted a rather objectionable odor. In the present study in which heating temperatures were kept below 160° C., some objectionable odor was noticed during plasticization and application, but none was observed after

application. Probably, the objectionable odor reported by Duecker and Schofield (5) resulted from decomposition caused by higher processing temperatures.

The service performance of the traffic stripes described in this article was determined under rather severe conditions. The object of the project was to develop a more suitable material for the yellow dash stripe parallel to and immediately adjacent to the highway center stripe, but all test stripes were laid at right angles to the center stripe. In all cases of slight or moderate loss by traffic abrasion, practically all such loss occurred in the rather narrowly defined tire lanes where the traffic load was high. Other portions of these stripes were subjected to occasional traffic loads, which were, however, probably more frequent than the traffic loads received close to and parallel to the center line. Usually, in such cases, no loss occurred in the 1- to 2-foot sections next to the center line and next to the curb.

#### SUMMARY

Performance tests with plasticized sulfur compositions indicate that such materials are promising as traffic marking materials. Optimum results are obtained with a sulfur composition containing 5 to 15% of Thiokol Type A, 1 to 3% of a Hansa Yellow type pigment, and 0.5% of a suitable bactericide. The incorporation of glass beads results in fairly good light reflectance; beading increases the effective life of the material. The results of recent tests, which will require longer observation, indicate that the incorporation of about 2% of wood rosin is significantly beneficial. The rosin has an auxiliary plasticizing action which results in better retention of bond to the pavement and smaller loss by fracture from traffic loads.

Traffic stripes laid with such materials show a good initial yellow color, but early traffic discoloration occurs; however, the initial color is restored to some extent by weathering and traffic abrasion. The use of surface drying materials for correcting the early traffic discoloration should be investigated.

These plastic sulfur compositions show about the same performance on both asphalt and concrete pavements. With Thiokol Type A contents of 5 to 15%, the setting-up time in minutes required before opening to traffic is very roughly equal to the percentage of Thiokol. The film thickness can be controlled well with compositions containing 8 to 15% of Thiokol, but with 5% or less, considerable spreading after laying occurs.

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## LITERATURE CITED

- (1) Bacon, R. F., and Fanelli, R., *J. Am. Chem. Soc.*, **65**, 639 (1943).
- (2) Beckwith, T. D., and Bovard, P. F., *Chem. & Met. Eng.*, **40**, 530 (1933).
- (3) Duecker, W. W., private communication, Oct. 28, 1952.
- (4) Duecker, W. W., and associates, *J. Am. Water Works Assoc.*, **40**, 715 (1948).
- (5) Duecker, W. W., and Schofield, H. Z., *Bull. Am. Ceram. Soc.*, **16**, 435 (1937).
- (6) Frederick, L. R., and Starkey, R. L., *J. Am. Water Works Assoc.*, **40**, 729 (1948).
- (7) Highway Research Board, Washington, D. C., "Pavement-Marking Materials," *Bull.* 57 (1952).
- (8) Keese, C. J., *Roads and Streets*, **95**, No. 10, 56 (1952); *Texas Eng. Expt. Sta., Bull.* 130 (March 1953).
- (9) Keese, C. J., and Benson, F. J., Highway Research Board, *Bull.* 57, 49 (1952).
- (10) Kobbe, W. H., U. S. Patent 1,655,504 (Jan. 10, 1928).
- (11) Koebig, J., *Ibid.*, 1,577,729 (March 23, 1926).
- (12) Massa, A. P., Colon, H., and Schurig, W. F., *IND. ENG. CHEM.*, **45**, 775 (1953).
- (13) Rueckel, W. C., and Duecker, W. W., *Bull. Am. Ceram. Soc.*, **14**, 329 (1935).
- (14) Schulze, W. A., Short, G. H., and Crouch, W. W., *IND. ENG. CHEM.*, **42**, 916 (1950).
- (15) White, R. S., private communication, Dec. 1, 1953.

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# Sulfonation Products from Polymers of Styrene and Vinyltoluene .

H. H. ROTH

Physical Research Laboratory, The Dow Chemical Co., Midland, Mich.

THE tonnage quantity production of polystyrene, as well as its low price, has made it look attractive as a starting material for a new synthetic gum. Coupled with this is the further potential lowering of price due to the use of low-priced sulfonating agents which are available to convert the polystyrene to water-soluble products (98% sulfuric acid at 1 cent, chlorosulfonic acid at 4 cents, and sulfur trioxide at 3 cents). As a synthetic gum the sulfonation products should find application as aqueous thickeners, impregnants, adhesives, and textile sizes. They may be produced as a white powder which readily dissolves in cold water. Their solubility is little affected by acid, alkali, or temperature. Because they are polyelectrolytes, they also have potential application in soil conditioning. It was the potential wide utility of the sulfonation products that attracted this laboratory to studies in this field.

Because of the competitiveness of the market today, a new synthetic gum will be required to meet rather stringent specifications. One of these will be water viscosity. As sulfone crosslinking during sulfonation will cause the water viscosity of the sulfonation products to vary over an extremely wide range of values, it is of great importance to prevent the side reaction, particularly where commercial production is desired. Heretofore it was deemed necessary to sulfonate only to the extent of water solubility in order to have a marketable product, while the problem of crosslinking was almost universally ignored. The present lack of commercialization is probably due to an inability of known sulfonation processes to prevent or control this crosslinking. Not only is the prevention of crosslinking necessary from a processing viewpoint, but the noncrosslinked products are also more desirable. They have a molecular configuration which is the same as the well known polystyrene molecule, their water viscosity is dependent upon the molecular weight of the starting polymer, and their behavior as a polyelectrolyte becomes predictable.

The sulfonation of polystyrene to produce water-soluble products has been the subject of several patents (1, 2, 7, 16, 17, 21, 23). These patents and others (3, 4, 8, 9, 11, 13, 15) show the potential, and some proved, utilities of the sulfonation products. Also of interest should be the patents concerning sulfonation products of copolymers of styrene and maleic anhydride (10) and of polymethylstyrene (19). Of the considerable literature now available on this subject, almost all is contained in patents. Only one paper has been published to date on the subject—the

excellent work of Signer and Demagistri (18) which discusses the properties of noncrosslinked sulfonic acid derivatives of a molding grade polystyrene. Jones (12) discusses the production of other water-soluble derivatives of polystyrene by chloromethylation and subsequent amination.

This paper discusses further the production of noncrosslinked sulfonation products of molding grade polystyrene as well as other products of comparable linearity. The products under discussion could not be produced in the author's laboratory by any of the methods of sulfonation taught in the available patents (1, 2, 7, 16, 17, 21, 23). It was only upon the development of a new sulfonation technique (mixed solvents of Method B) that it became possible to sulfonate polystyrenes without undue crosslinking.

## METHODS OF SULFONATION

**METHOD A.** Dissolve 10 grams of Styron 666 in 480 ml. of dry carbon tetrachloride. Adjust to the desired temperature and agitate in a jacketed Waring Blendor jar with blades rotating at about 1650 r.p.m. To this solution add 200 ml. of dry carbon tetrachloride containing 6.6 ml. of monomeric sulfur trioxide over about a 10- to 15-minute period of time. Dry nitrogen is blanketed over the surface of the solvent to minimize moisture pickup during the sulfonation. Allow the slurry to agitate for 10 minutes after the sulfur trioxide solution has been added. Drain the excess carbon tetrachloride from the sulfonation product. Immediately disperse the product in dry ether. Several extractions are necessary to purify to a sulfuric acid-free product. The final product is a white powder of low volume density.

**METHOD B.** Dissolve 10 grams of Styron 666 in 300 ml. of dry carbon tetrachloride. Transfer the solution to a glass-lined pressure vessel containing an agitator. To the solution in the sealed pressure vessel add 240 ml. of liquid sulfur dioxide under pressure. Adjust the contents in the vessel to the desired temperature and agitate at about 2200 r.p.m. To the polymer solution add 400 ml. of liquid sulfur dioxide containing 6.6 ml. of substantially pure monomeric liquid sulfur trioxide over a 5- to 10-minute period. Agitate further for 10 minutes and then cool the vessel to below  $-10^{\circ}\text{C}$ . Remove the slurry, filter, and purify the sulfonation product in dry ether. The final product is a white powder of low volume density.

**METHOD C.** The sulfonation temperature of about  $-10^{\circ}\text{C}$ . allows the handling of liquid sulfur dioxide in open vessels. At this temperature it was found desirable to modify Method B to a concurrent reactant feed mode of sulfonation. This minimizes