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ANTIFLEX-CRACKING AGENTS IN RUBBER

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6 Claims. (Cl. 260—810)

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This invention relates to the stabilization of natural rubber by the incorporation therein of a material which prevents or inhibits cracking of the rubber on flexing. The flex-cracking inhibitor employed is a cresylic acid alkylated with introduction of at least about one, and generally no more than about two, hydrocarbon substituents of four to twelve carbon atoms for each molecule of the acid. It has been found that the alkylated cresylic acids do not discolor rubber as do the most commonly used commercial flex-cracking inhibitors. These badly discolor light-colored rubbers, such as the white sidewalls of tires and other rubbers heavily loaded with white pigment.

Cresylic acids are obtained from petroleum sources and also from coal and wood derivatives, as by the treatment of coal- and wood-tar distillates. They are available in large quantity and are relatively inexpensive. The term "cresylic acid" is used to designate a mixture of phenolic materials, particularly cresols, xylenols, trimethylphenols, tetramethylphenols, ethylphenols and methylethylphenols, and also some higher homologues. The higher homologues include at most no more than a trace of any propyl or higher alkylphenol.

One method of obtaining petroleum cresylic acid is to extract a cracked petroleum distillate with aqueous caustic soda and thus obtain the salts of the mixture of acids which go to make up the cresylic acid. The resultant solution containing some dissolved oil separates from the distillate by settling. This oil is removed by steam distillation, and the residual solution is acidified to free the cresylic acid which, on standing, rises to the top of the water solution. The acid is then usually recovered by distillation in a vacuum, and it is customary to separate the distillate into fractions of different boiling ranges. These may be further purified if desired. The total acid includes cresols, ethyl-, dimethyl-, trimethyl-, and tetramethylphenols. It contains no more than a trace, if any, of a phenol alkylated with a group which contains three or more carbon atoms.

The mixture of acids in the lower boiling fraction of a cresylic acid, whether it be derived from petroleum, coal or wood, is of the same general composition. This is true of the cresylic acids which boil from 190° to 250° C. at atmospheric pressure. The alkylation derivatives of

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such acids form the preferred stabilizers of this invention.

The compositions of the higher boiling fractions are quite different. The higher cuts of coal-tar cresylic acids—for example, those boiling above about 250° C.—contain fused ring compounds, such as naphthols, etc. The alkylation derivatives of these higher boiling coal-tar cresylic acid fractions are not as desirable for use in rubber as the alkylation derivatives of the higher cuts of petroleum cresylic acids. The latter are also preferred to the alkylation derivatives of the higher cuts of the wood-tar cresylic acids.

The boiling range of the alkylated cresylic acids varies. In general, it may be said that these compounds have an initial boiling point of at least 100° C. at 10 mm. pressure. If a butylene—for example, isobutylene, is used for the alkylation, the reaction product will begin to boil at about 100° C. under 10 mm. pressure. If diisobutylene is used the initial boiling point will be in the neighborhood of about 120° C. at 10 mm. pressure.

Thus, the stabilizers of this invention are alkylated cresylic acids. Although a higher boiling fraction of a petroleum cresylic acid may be used for the alkylation, or a higher cut of an alkylated petroleum cresylic acid may be used, and is included within the scope of this invention, the invention relates more particularly to the use of alkylated lower cuts of those cresylic acids which boil at not over 250° C., and these preferred inhibitors may be derived from any alkylated cresylic acid whether of petroleum, coal or wood origin. Of those acids which boil at 250° C. and below, the lower boiling constituents are more easily alkylated than the higher boiling, and because of the ease with which they can be prepared they are generally preferred to the more difficultly alkylated, higher boiling constituents. Whatever fraction of the cresylic acids is employed, and whatever the process of alkylation, it results in introduction of substantially one to two alkyl groups per molecule.

In certain of the following examples the boiling range of the unalkylated starting material overlaps the boiling range of the alkylated product. It does not follow that the alkylated product contains any considerable percentage of unalkylated material, because the lower boiling alkylated cresylic acids boil within the range of

the higher boiling unalkylated cresylic acids. Actually, unalkylated cresylic acid has little stabilizing action on natural rubber, whereas the alkylated product is a very effective stabilizer. Moreover, the unalkylated material is more volatile and has an offensive odor not present in the alkylated product. In the claims the boiling range attributed to the alkylated product has been selected to avoid overlapping, because the percentage of products in the range of the overlap is inappreciable and it would be impractical commercially to use a fraction of such limited boiling range.

Alkylation may be effected with isobutylene, diisobutylene, triisobutylene, dipropylene, tripropylene, tetrapropylene, mixed heptenes, mixed actenes, mixed nonenes, mixed decenes, undecenes, or other olefin or a mixture of olefins, or by a Friedel-Crafts reaction using an alkyl halide of three or more carbon atoms, such as a chloro- or bromo-derivative of n-butane, isobutane, any pentane, hexane, heptane, octane, nonane, decane, etc., or a mixture thereof. In general, the stabilizers will contain no alkyl group higher than dodecyl. Any suitable method of alkylation may be employed, such as the use of an aliphatic alcohol corresponding to the olefins or alkyl halides mentioned above, etc.

The following examples illustrate the preparation of the alkylation derivatives.

EXAMPLE 1

This illustrates the alkylation of a higher-boiling cresylic acid, boiling at not over 250° C.

One hundred grams of petroleum cresylic acid (B. P. 221–245° C. at atmospheric pressure or 98 to 118° C. at 10 mm.) mixed with 50 g. toluene as diluent, and as catalyst, 40 g. of 1:1 mixture of conc. sulfuric acid and anhydrous glycerine, was maintained at 70 to 75° C. for three hours while a stream of isobutylene was passed through it. The upper layer was then decanted from the catalyst solution, washed with water and with sodium carbonate solution, and then distilled to yield 127 g. of light yellow liquid of $n_D^{24}=1.5198$ and B. P. 101–157° C. at 10 mm.

The above preparation was fractionated and the following two fractions alkylated further:

One hundred grams of the fraction boiling 100–120° at 10 mm. was stirred with 20 g. aluminum chloride while 190 g. of tert-butyl chloride was run in with stirring over six hours at 38–44° C. The reaction mixture was poured into water, the product extracted with petroleuum ether and washed with successive portions of sodium bicarbonate solution, sodium carbonate solution and water. After removal of solvent, the product was distilled, the portion boiling from 103° at 10 mm. to 210° at 4 mm. being blended with the final product from the second fraction.

One hundred grams of the fraction boiling between 120–156° C. at 10 mm. was mixed with 20 g. of aluminum chloride and stirred at 37–45° while 200 g. of tert-butyl chloride was run in over three hours. After an additional five hours of stirring the reaction mixture was poured into water, extracted with petroleum ether and washed with successive portions of sodium bicarbonate solution, sodium carbonate solution and water. After drying over anhydrous sodium sulfate and removal of solvent the product was distilled, the material boiling from 110° C. at 10 mm. to 193 at 3 mm., being combined with the alkylated lower fraction described in the previous paragraph.

The resulting blend boiled at 100° C. at 10 mm. to 210° C. at 4 mm. and was used in natural rubber as described below.

EXAMPLE 2

The following example illustrates the octylation of a lower-boiling cresylic acid.

One hundred grams of petroleum cresylic acid (B. P. 195–228° C. at atmospheric pressure or 82 to 106° C. at 10 mm.) and 10 grams of boron fluoride etherate were stirred at 40–75° C. while 200 gr. of diisobutylene was dropped in over one hour. Stirring was continued for two hours and the mixture allowed to stand 15 hours at 55–60° C., after which it was washed with sodium carbonate solution, then with aqueous sodium hydroxide, and lastly with water. The octylcresylic acid thus obtained was diluted with ether, dried over anhydrous potassium carbonate and distilled. B. P. 140° C. at 10 mm. to 167° C. at 3.5 mm. Yield 93 g.

Carbon and hydrogen analysis:

	Per Cent C	Per Cent H
Calculated for monooctyl cresylic acid	82.0	11.1
Calculated for dioctyl cresylic acid	83.0	12.1
Found	81.71	11.54

EXAMPLE 3

The cresylic acid used in this preparation is a petroleum cresylic acid fraction with a boiling range of 92 to 121° C. at 10 mm. or 210–250° C. at 760 mm. It is substantially the same cut as used in Example 1.

One hundred grams of the acid were mixed with 200 grams of diisobutylene. Forty grams of a 1:1 mixture of sulfuric acid and anhydrous glycerol was added as the catalyst at 5 to 10° C. The reaction mixture was stirred for four hours at 5 to 10° C., and then it was washed to remove the catalyst. After drying over anhydrous sodium sulfate, the octylcresylic acid thus obtained was distilled. Thirty-seven grams of product was taken at 122 to 166° C. at 10 mm. Such a product was used in the following tests.

The several inhibitors were incorporated in a white rubber stock such as the following:

	Parts by weight
Crepe rubber	100
Wax	2
Zinc oxide	72
Titanium dioxide	20
Ultramarine blue	0.1
Sulfur	3
Stearic acid	1
Accelerator	1
Inhibitor	1

The compounds were cured and tested against a blank which was similarly compounded, but contained no inhibitor. The several samples were subjected to a flexing test in which ½-inch dumbbell strips of 0.100 gauge were flexed from 0 to 75 per cent elongation until all strips were broken. The strips were then examined under a magnifying lens and the number of cracks estimated. Totaling the number of hours required for the strips of each different stock to break, the flex life was obtained. From the total number of cracks and the total number of hours run, the average rate of crack formation was calculated. The results of the tests on the various stocks are recorded in the following table. The inhibitors are identified simply by reference to the examples which describe how they may be prepared.

Inhibitor	Flex Life, Hours	Improvement	Rate of Crack Formation	Improvement
		Per cent		*Per cent*
Example 1	68.08	64	1.6	53
Blank	41.42		3.4	
Example 2	31.70	41	7.2	61
Blank	22.53		5.8	
Example 3	46.33	44	2.8	57
Blank	32.48		6.5	

These stocks were exposed to weathering tests. Stocks containing inhibitors such as obtained by the processes of Examples 1 and 3 were weathered 8 weeks in Florida. The test stocks and blanks remained white. Stock containing the stabilizer described in Example 2 was exposed to 18 weeks of California weather. Both the under surface of each sample, exposed to indirect sunlight, as well as the upper surface, exposed to direct sunlight, were examined and found not to have discolored. The blank showed more surface cracks than the test stock.

EXAMPLE 4

A petroleum cresylic acid was alkylated to produce the product known herein as Example 4. Fractions of the product are identified herein as Examples 4A, 4B and 4C. Their various boiling ranges are given in the table below.

Sixty pounds of petroleum cresylic acid (B. P. 195 to 225° C. at atmospheric pressure; 82 to 102° C. at 10 mm. pressure) and 50 pounds of diisobutylene were stirred at 60–70° C. while 4 pounds of boron fluoride etherate was run in during the course of one hour. After two hours continued stirring at 65–70° C. the mixture was allowed to stand over night. It was then washed with water, and aqueous solution of sodium bicarbonate and sodium sulfite, and again with water. The product was then distilled, first under atmospheric pressure, then under reduced pressure. The material distilling at 140–173° C. at 10 mm. was taken as the product of Example 4. Fractions obtained are identified in the following table:

Example	Boiling Range
4	140–173° C./10 mm.
4A	140–152° C./10 mm.
4B	152–163° C./10 mm.
4C	164–173° C./10 mm.

The various products were incorporated in crude rubber according to a formula such as the above, and the stocks were cured. Samples containing fractions 4A, 4B and 4C cured at 280° F. for different periods of time were exposed to a General Electric sunlamp of the R–S type at a distance of 7 inches for 16 hours together with rubber similarly compounded but containing no stabilizer. The results are recorded in the following table:

Exposure to sun lamp

Stabilizer	Length of Cure			
	20 Minutes	40 Minutes	60 Minutes	80 Minutes
4A	Slightly creamy.	Very slightly creamy.	White	White.
4B	do	do	do	Do.
4C	do	do	do	Do.
Blank	do	Slightly creamy.	do	Do.

The above is evidence that the alkylated cresylic acids do not deepen the color of the cured rubber compound. These stabilizers therefore belong to the non-discoloring type.

Samples of the cured rubber were tested also against the blank containing no stabilizer, in order to determine the effect of the various stabilizers on the flex life of the rubber. Eight strips were used in each test, 2 strips being cured at 280° F. for 20 minutes, 40 minutes, 60 minutes and 80 minutes respectively. The results are recorded in the following tables:

Stabilizer	Flex-Life, Hrs.	Improvement
		Per cent
Example 4	121.27	56
Example 4B	125.35	62
Blank	77.60	

The other stabilizers were similarly tested against a blank with the following results:

Stabilizer	Flex-Life, Hrs.	Improvement
		Per cent
Example 4A	82.93	57
Example 4C	90.32	71
Blank	52.70	

These test results show that the stabilizers definitely inhibit flex-cracking.

EXAMPLE 5

A petroleum cresylic acid was nonylated and used as a stabilizer in rubber with very satisfactory results. Certain of the tests made on this product are recorded below.

The stabilizer was prepared from a petroleum cresylic acid having a boiling range of 193 to 220° C. at atmospheric pressure, (78 to 98° C. at 10 mm.). Three hundred grams of the acid and 300 grams of a mixture of nonenes (obtained by polymerization of propylene) were treated with 30 grams of boron trifluoride-ether complex. The temperature of the reaction mixture rose to 35° C. The reaction mixture was heated at 60–65° C. for two hours. After cooling it was washed with water, with a 2 per cent sodium sulfite-2 per cent sodium bicarbonate mixture, and finally with water. The crude yield of 610 grams was distilled under reduced pressure. The forefraction up to 140° C. at 10 mm. contained 365 grams of material. The product was taken at 140° C. at 10 mm. to 205° C. at 3.5 mm., and weighed 235 grams (n_D^{25}=1.5145).

The forefraction was treated with 50 grams of anhydrous aluminum chloride. Addition of the aluminum chloride caused the temperature to rise to 80° C. and then the reaction mixture was heated at 100–110° C. for two hours. After washing with water, with 2 per cent sodium bicarbonate and 2 per cent sodium sulfite, and water, the product was distilled. The forefraction (up to 140° C./10 mm.) weighed 165 grams. The product was taken at 140° C. at 10 mm. to 250° C. at 2 mm. and weighed 165 grams (n_D^{25}=1.5156). This yield was 27.5 per cent of the total reactant weight. Hence, the combined yield was 66.7 per cent of the total reactant weight.

This nonylated cresylic acid was compounded with rubber according to the following formula:

	Parts by weight
Pale crepe rubber	100.0
Zinc oxide	85.0
Titanium dioxide	10.0
Insoluble sulfur	3.0
Ultramarine blue	0.2
Stearic acid	1.2
Dibutyl ammonium oleate	0.5
Benzothiazolyl disulfide	0.4
Sunproof wax	2.0
Stabilizer	1.0

The material compounded according to the above formula was tested for comparison with a blank similarly compounded but omitting the stabilizer. Cures were made at 280° F. for 20, 40, 60 and 80 minutes. The two vulcanizates were tested with the following results:

NORMAL TENSILE PROPERTIES

	Blank	Test material
		Pounds per sq. inch
Modulus at 500%:		
20 min. at 280° F.	1550	1500
40 min. at 280° F.	1875	1825
60 min. at 280° F.	1775	1700
80 min. at 280° F.	1575	1575
Tensile Strength:		
20 min. at 280° F.	3525	3550
40 min. at 280° F.	3500	3450
60 min. at 280° F.	3200	3175
80 min. at 280° F.	3175	2925
		Per cent
Elongation at Break:		
20 min. at 280° F.	675	680
40 min. at 280° F.	620	625
60 min. at 280° F.	610	620
80 min. at 280° F.	635	615

TENSILE PROPERTIES AFTER AGING TWO DAYS AT 212° F.

		Pounds per sq. inch
Modulus at 500% Elongation:		
20 min. at 280° F.	1700	2050
40 min. at 280° F.	2000	2075
60 min. at 280° F.	1950	1900
80 min. at 280° F.	1825	1800
Tensile Strength:		
20 min. at 280° F.	2100	2600
40 min. at 280° F.	2200	2075
60 min. at 280° F.	2175	2050
80 min. at 280° F.	2150	2125
		Per cent
Elongation at Break:		
20 min. at 280° F.	540	555
40 min. at 280° F.	520	500
60 min. at 280° F.	520	520
80 min. at 280° F.	520	520

RETAINED TENSILE STRENGTH

Per cent	64	68
Index	100	106

The two cured rubber samples were subjected to flexing after having been aged two days at 212° F. and the material containing the stabilizer was found to have a flex life 10 per cent longer than the blank. The number of cracks produced was much less in the material containing the stabilizer, in the ratio of 167:130.

The two samples of rubber, each cured at 40 and 60 minutes, were subjected to four hours treatment in an artificial weathering machine with the following results:

Nature of Cure	Blank	Test Material
40 min. at 280° F.	White	Very light cream.
60 min. at 280° F.	do	White.

The above tests show that nonylated cresylic acid is an effective stabilizer in natural rubber and substantially non-discoloring.

The stabilizers of this invention are alkylated to an appreciable degree. The extent to which alkyl substituents are introduced into the cresylic acid will vary with the nature of the alkylation process employed, etc. In general, it may be said that for each molecule of the stabilizer there are, on the average, one to two alkyl substituents each comprising four to twelve carbon atoms.

By a study of hydroxyl numbers the number of alkyl substituents added per molecule of cresylic acid, on the average, by certain of the above processes, has been determined. The unalkylated acid contains no more than a trace of any substituent with four or more carbon atoms. The number of such substituents added is, therefore, for all practical purposes, the amount of such substituents present.

Thus, the calculated hydroxyl numbers for mono- and di-octylated cresylic acids average 7.23 and 4.91, respectively, whereas the calculated hydroxyl numbers of the starting cresylic acids themselves vary within the range of 12.5 to 15.7. The hydroxyl numbers for the products identified as Examples 4, 4A, 4B and 4C were found to 7.47, 6.60, 6.30 and 4.75 respectively. The calculated numbers are based on approximations, and within the limits of experimental error it is shown that the octylated cresylic acid and its fraction average one to two octyl substituents per molecule.

The calculated hydroxyl numbers for the mono- and di-nonylated cresylic acids are 6.82 and 4.53. That found for the stabilizer of Example 5 was 5.77.

The examples and tests are representative. The invention is not limited thereto. Other alkylated cresylic acids comprising for each molecule, one to two alkyl groups each containing four to twelve carbon atoms, and with an initial boiling point no lower than 100° C. at 10 mm. pressure, and derived from cresylic acids boiling at temperatures of 190 to 250° C. at atmospheric pressure are likewise good inhibitors and are included within the scope of this invention; and petroleum cresylic acids of any boiling range containing one to two such alkyl groups per molecule are stabilized and included in the invention. Any formula for sulfur vulcanization may be used. The stock need not be heavily loaded with white pigment. From 0.10 to 10 per cent of the inhibitors may be employed, and they may be used in conjunction with other stabilizers.

What I claim is:

1. Cured natural rubber which contains as flex-cracking inhibitor a small amount of a cresylic acid alkylated by introduction of one to two hydrocarbon substituents of four to twelve carbon atoms per cresylic acid molecule, the alkylated cresylic acid being constituted of a mixture of compounds which boils above 100° C. at ten millimeters pressure and being derived from cresylic acid boiling at 190° to 250° C. at atmospheric pressure.

2. Cured natural rubber which contains as flex-cracking inhibitor a small amount of a petroleum cresylic acid alkylated by introduction of one to two hydrocarbon substituents of four to twelve carbon atoms per cresylic acid molecule, the alkylated cresylic acid being constituted of a mixture of compounds which boils above 100° C. at ten millimeters pressure and being derived from petroleum cresylic acid boiling at 190 to 250° C. at atmospheric pressure.

3. The process of curing natural rubber which comprises heating the same with sulfur and as a flex-cracking inhibitor a small amount of a cresylic acid alkylated by introduction of one to two hydrocarbon substituents of four to twelve carbon atoms per molecule of cresylic acid, the alkylated cresylic acid being constituted of a mixture of compounds which boils above 100° C. at ten millimeters pressure and derived from cresylic acid boiling at 190 to 250° C. at atmospheric pressure.

4. The process of curing natural rubber which comprises heating the same with sulfur and as a flex-cracking inhibitor a small amount of a petroleum cresylic acid alkylated by introduction of one to two hydrocarbon substituents of four to twelve carbon atoms per cresylic acid molecule, the alkylated cresylic acid being constituted of a mixture of compounds which boils above 100° C. at ten millimeters pressure and being derived from petroleum cresylic acid boiling at 190 to 250° C. at atmospheric pressure.

5. Vulcanizable but unvulcanized rubber composition which contains as flex-cracking inhibitor a small amount of cresylic acid alkylated by introduction of one to two hydrocarbon substituents of four to twelve carbon atoms per cresylic acid molecule, the alkylated cresylic acid being constituted of a mixture of compounds which boils above 100° C. at ten millimeters pressure and being derived from cresylic acid boiling at 190 to 250° C. at atmospheric pressure.

6. Vulcanizable but unvulcanized rubber composition which contains as flex-cracking inhibitor a small amount of petroleum cresylic acid alkylated by introduction of one to two hydrocarbon substituents of four to twelve carbon atoms per cresylic acid molecule, the alkylated cresylic acid being constituted of a mixture of compounds which boils above 100° C. at ten millimeters pressure and being derived from petroleum cresylic acid boiling at 190 to 250° C. at atmospheric pressure.

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CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 49, for "stabilized" read -- stabilizers --.

Signed and sealed this 29th day of October 1957.

(SEAL)
Attest:
KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents