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(54) ANTIDEGRADANTS FOR RUBBER

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a corporation organised under the laws of Japan, of 15 Kitahama 5-chome, Higashi-ku, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to antidegradants for rubber, and more particularly to antidegradants which combat flex cracking and heat ageing in natural and synthetic rubbers.

Natural and synthetic rubber products generally crack on repeated flexing, and can become unsuitable for use due to growth of the cracks or to degradation by heat.

Various attempts have been made to prevent such flex cracking and heat ageing, many by use of phenyl-β-naphthylamine or diphenylamine derivatives as antidegradants.

With these antidegradants, however, satisfactory performance has not yet been obtained. In recent years there have been increasing demands for improvement in the flex cracking resistance and heat ageing resistance of rubber compounds with increased production of radial tires and belts for high-speed belt conveyors, and for this reason, there have also been strong demands for the development of antidegradants having good performance in preventing flex cracking and heat ageing.

2,2,4-trimethyl-1,2-dihydroquinoline polymer mixture, the so-called dihydroquinoline polymer produced by reaction between aniline and acetones, is widely used as a heat ageing resistant, since it is not only effective in preventing heat ageing but is also economical and readily available. It is known from gas-chromatography (internal standard method) that the main component of antidegradants now on the market as the so-called dihydroquinoline polymer is a mixture of 2,2,4-trimethyl-1,2-dihydroquinoline trimer and more highly polymerised products than the trimer, and in addition thereto large amounts of impurities having no dehydroquinoline structure are contained. Since commercial dihydroquinoline polymer antidegradant has little or no effect in preventing flex cracking, it is at present necessary to use a flex cracking resistant in combination with it in order to prevent both flex cracking and heat ageing; furthermore the said polymer causes various practical problems - for example it has such poor compatibility with rubbers as to cause problems in rubber processing.

We have surprisingly found that, of the various polymers of 2,2,4-trimethyl-1,2-dihydroquinoline, the dimer alone shows superior ability to prevent flex cracking, particularly at high temperatures, and improves resistance to degradation by heat or oxidation, and moreover that the dimer is compatible with rubbers. We have further found that even mixtures comprising the said dimer, the said dihydroquinoline monomer and more highly polymerised products than the said dimer display ability to prevent both heat and oxidation ageing and flex cracking in rubber when the dimer content of the mixtures is 25% by weight or more.

The present invention provides an antidegradant for rubber comprising a mixture consisting essentially of 2,2,4-trimethyl-1,2-dihydroquinoline monomer (referred to as "quinoline monomer" hereinafter), dimer thereof (referred to as "quinoline dimer" hereinafter) and more highly polymerised products than the said dimer (referred to as "quinoline polymer" hereinafter), the contents of the said quinoline monomer and the said quinoline dimer being less than 5% by weight and 25% by weight or more, respectively, and

also provides a method for combating heat ageing and flex cracking of rubber at the same time by incorporating said antidegradant into rubber.

5 The method of production of the antidegradant of the present invention is not critical. For example, it may be produced by reacting aniline and acetones (e.g. acetone, diacetone alcohol, mesityl oxide) in the presence of an acidic catalyst by usual methods [for example, D. Craig; J.C.S., 60 1458 (1938)], under reaction conditions (such as catalyst amount and reaction temperature) adjusted so as to produce the said mixture containing at least 25% by weight of the quinoline dimer. They may be produced instead by mixing appropriate amounts of the quinoline dimer, the quinoline monomer and the quinoline polymer which have been performed by usual methods. 10

In the antidegradants of the present invention, the content of the quinoline dimer is at least 25% by weight, preferably at least 35% by weight, more preferably at least 50% by weight. Further, use of the quinoline dimer per se, e.g. produced by removing the quinoline monomer and quinoline polymer from the reaction product described above, is of course included in the present invention. 15

The antidegradants of the present invention can be incorporated not only in natural rubber but also in synthetic rubbers such as styrene/butadiene copolymer rubbers, acrylonitrile/butadiene copolymer rubbers, polybutadiene rubbers and polyisoprene rubbers by usual methods, for example using mixers such as mixing rolls and Banbury mixers. The amount of antidegradant incorporated is generally 0.1 to 7 parts by weight, preferably 0.2 to 4 parts by weight, per 100 parts by weight of rubber. 20

Other additives and antidegradants such as N-phenyl-N'-alkyl-p-phenylenediamines and N,N'-diaryl-p-phenylenediamines may be included in rubber along with the antidegradant according to the invention.

25 The present invention is illustrated by the following specific Examples, which are not however to be interpreted as limiting the present invention. In the Examples, all parts are by weight.

Example 1

30 A rubber compound containing 100 parts of natural rubber, 45 parts of HAF carbon, 5 parts of zinc oxide, 2.5 parts of sulfur, 1 part of stearic acid, 5 parts of a process oil, 0.5 parts of N-cyclohexylbenzothiazylsulfenamide (vulcanization accelerator) and 1 part of an antidegradant shown in Table 1 was milled as usual on a 6 inches ϕ mixing roll. The rubber sheet thus prepared was tested for tackiness. The same rubber compound was vulcanized at 140°C. for 30 minutes and the vulcanized rubber product was subjected to a heat ageing test and a flex cracking test. 35

Tackiness between rubbers was measured on a Tel-Tak meter (produced by Monsanto Co.) using the test piece which had been prepared by cutting the above mentioned rubber sheet in 5 mm. widths and ageing at 25°C. for 10 days. The heat ageing test was carried out according to JIS K 6301, i.e. by heat-ageing the test pieces at 100°C. for 24 hours in a test tube heat ageing tester, and then measuring physical properties of the resulting test pieces. 40

The flex cracking test was carried out as follows according to JIS K 6301: a hole of 2 mm. in length is made vertically through the test piece, and, after the required number of times of flexing, the length of crack is measured.

45 The same test was also applied to test pieces which had been heat-aged at 100°C. for 24 hours in a gear oven. 45

The results obtained are shown in Table 2. It is apparent from the table that the antidegradants of the present invention have a high tackiness and good compatibility with rubbers and further that they are very superior in heat ageing resistance and flex cracking resistance. 50

TABLE 1

5	Experiment No.	Composition (weight %) *			5	
		Quinoline dimer	Quinoline monomer	Other reaction products		
10	1	96	1	3	10	
	2	76	2	22		
	3	52	4	44		
15	Example	4	42	2	56	15
	5	36	3	61		
	6	28	4	68		
20	-----					20
	7	18	1	81		
25	Comparative Example	8	13	2	85	25
	9	Phenyl- β -naphthylamine				
	10	Condensation product of diphenylamine and acetone				

30 *The composition was measured under the following conditions according to the internal
standard method of gas-chromatography: 30

35	Apparatus	: GC-163 (produced by Hitachi Seisakusho Co.)	35
	Column	: Silicone OV-1 ("Chromosorb" W, AW, DMCS) 3mm ϕ \times 1m. "Chromosorb" is a Registered Trade Mark).	
	Temperature	: Constant temperature vessel 110 - 300°C. (10°C./min.) Inlet 300°C. Detector 300°C.	
40	Detector	: FID	40
	Carrier gas	: N ₂ (0.6 kg./cm ²)	
	Internal standard substance	: Di-n-butyl phthalate	

45 In this case, the retention time ratio of the quinoline dimer to di-n-butyl phthalate was 1.9
to 2.1 and that of the quinoline monomer to di-n-butyl phthalate was 0.2 to 0.3. The
structures of the quinoline dimer and quinoline monomer were identified using a mass
analysis apparatus and nuclear magnetic resonance absorption apparatus. 45

Example 2

A rubber compound containing 100 parts of styrene/butadiene rubber, 50 parts of HAF carbon, 5 parts of a process oil, 5 parts of zinc oxide, 3 parts of stearic acid, 2.5 parts of sulfur, 1 part of N-cyclohexylbenzothiazylsulfenamide (vulcanization accelerator) and 1 part of an antidegradant shown in Table 1 was milled as usual on a 6 inches ϕ mixing roll and vulcanized at 145°C. for 30 minutes. Using the test pieces thus obtained, a flex cracking test was carried out in the same manner as in Example 1. The results obtained are shown in Table 3.

TABLE 3

Experiment No.	Example										Comparative Example
	1	2	3	4	5	6	7	8	9	10	
(Before heat ageing)											
Length of crack after 3000 bendings (mm)	4.8	5.0	5.1	5.2	5.2	5.3	5.7	6.8	5.3	5.3	5.3
Length of crack after 5000 bendings (mm)	8.0	8.3	8.4	8.5	8.6	8.6	9.9	10.2	9.0	9.0	9.0
(After heat ageing)											
Length of crack after 3000 bendings (mm)	7.7	8.2	8.3	8.4	8.5	8.5	9.3	10.0	8.6	8.6	8.7
Length of crack after 5000 bendings (mm)	12.6	13.2	13.4	13.5	13.5	13.6	14.4	15.3	13.8	13.8	14.0

WHAT WE CLAIM IS:-

1. An antidegradant for rubber comprising a mixture of 2,2,4-trimethyl-1,2-dihydroquinoline monomer, dimer thereof and more highly polymerised product than the said dimer, the quinoline monomer and the quinoline dimer constituting respectively less than 5% by weight and at least 25% by weight of the mixture. 5
2. An antidegradant according to Claim 1 wherein the said mixture is one produced by reacting aniline and ketone in the presence of an acidic catalyst. 5
3. A method for combating heat ageing and flex cracking of rubber which comprises incorporating into the rubber as antidegradant (a) 2,2,4-trimethyl-1,2-dihydroquinoline dimer in the absence of its monomer and higher polymers, or (b) a mixture of the said dimer with its monomer and/or higher polymers, the mixture containing at least 25% by weight dimer and less than 5% by weight monomer. 10
4. A method according to Claim 3 wherein the amount of the antidegradant incorporated is 0.1 to 7 parts by weight per 100 parts by weight of rubber. 15
5. A method according to Claim 3 or 4 wherein the rubber is selected from natural rubber, styrene/butadiene copolymer rubbers, acrylonitrile/butadiene copolymer rubbers, polybutadiene rubbers and polyisoprene rubbers. 15
6. An antidegradant for rubber comprising a mixture of 0-5%, 2,2,4-trimethyl-1,2-dihydroquinoline monomer, at least 25% dimer thereof, and higher polymer thereof, the percentages being based on the weight of the said mixture. 20
7. A rubber antidegradant substantially as hereinbefore described in any one of Examples 1 to 6. 20
8. A method of combating heat ageing and flex cracking of rubber, the method being substantially as hereinbefore described in any one of Examples 1 to 6. 25
9. A rubber composition containing as antidegradant 2,2,4-trimethyl-1,2-dihydroquinoline dimer in the absence of its monomer and higher polymers. 25
10. A rubber composition containing an antidegradant according to claim 1, 2, 6 or 7. 25
11. A composition according to claim 9 or 10 wherein the amount of the antidegradant incorporated is 0.1 to 7 parts by weight per 100 parts by weight of rubber. 30
12. A composition according to claim 9, 10 or 11 wherein the rubber is selected from natural rubber, styrene/butadiene copolymer rubbers, acrylonitrile/butadiene copolymer rubbers, polybutadiene rubbers and polyisoprene rubbers. 30
13. A rubber composition substantially as hereinbefore described in any one of Examples 1 to 6. 35

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