flavor than others. The plausibility of this suggestion is brought out by the data presented in Figure 2. When the different arcs are compared by computing the radiation of the region 2300–3100 Å. that would be required to develop a unit degree of activated flavor in milk, it becomes evident that substantially the same radiation of the region less than 2600 Å. is involved for all the arcs studied, whereas the radiation of the region 2600–3100 Å. is extremely variable. In order to keep the activated flavor to a minimum in the antirachitic activation of milk by irradiation, it would, therefore, seem advisable either to screen out radiation of short wave length or to select a source of radiant energy which has a low emission within the region less than 2600 Å. as compared with the emission in the region 2600–3100 Å.

A study similar to that described was made of flavor production by radiations of wave lengths greater than 3100 Å. Experimentally the radiations from the various arcs filtered through glass were allowed to act until a uniform unit intensity of flavor had been produced. By means of the relationship between the time of exposure and the intensity of the radiation, an estimation of the radiation expended was made as has been described. The data in Figure 3 show that, with all arcs, approximately the same amount of energy from the region 3100–3800 Å. had been used, whereas the amounts of radiation from 3800–7000 Å. varied considerably. Therefore, the conclusion appears justified that radiations ranging in wave length from 3100–3800 Å. are more responsible for production of flavor than those of 3800–7000 Å.

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Age Resisters in Vulcanized Rubber

Hydroxy-Substituted *N*-Phenyl Morpholines

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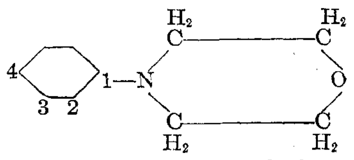
The hydroxy-substituted *N*-phenyl morpholines as a class are age resisters in vulcanized rubber. It is indicated that the hydroxyl group is most effective as an age resister when present in the 4- or para position. The position of the hydroxyl group or hydrocarbon radical in the molecule is important, the 2-methyl-4-hydroxy-*N*-phenyl morpholine causing the least staining. A hydrocarbon radical in the 3-position increases solubility in rubber.

In the general study of age resisters for rubber and other commercial materials, a number of hydroxy-substituted *N*-phenyl morpholines were prepared and tested. It was found that certain of the hydroxy-substituted *N*-phenyl morpholines are excellent age resisters (*3*), of activity comparable to that of phenyl-β-naphthylamine but with less staining in light-colored compositions.

The structure of the morpholines is probably not well known; therefore, the following structural formulas will suffice to describe these new compounds:



Phenyl morpholine or 4-phenyltetrahydro-1,4-oxazine

In general, the new compounds referred to in the paper are readily prepared by treating the proper aryl amine with β, β′-dichlorodiethyl ether in the presence of water and calcium carbonate at 100° C., with violent agitation.

Aging Tests

To illustrate the effectiveness of hydroxy-substituted *N*-phenyl morpholines compared with phenyl-β-naphthylamine and the unprotected control, physical tests of artificially aged rubber stocks are listed in Table I. The basic stock is a carbon black tread of low quality, chosen so that the effectiveness of an antioxidant would be apparent on the physical tests. The general recipe is as follows:

Rubber, smoked sheets No. 1	52.46	Palm oil	3.01
Sulfur	3.01	Mineral rubber	5.02
Zinc oxide	15.06	Hexamethylene tetramine	1.35
Carbon black	20.09	Age resister	0.50
			100.50

The oven-aging (*2*) consisted of exposing standard dumbbell test strips in a current of air at 70° C. for the period speci-

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fied. The Bierer-Davis aging (*1*) was carried out on similar strips at 70° C. and 21.1 kg. per sq. cm. oxygen pressure.

Staining Tests

A common fault of all active age resisters is that they discolor the surface of light-colored stocks exposed to direct sunlight or even to diffused daylight. To test the relative staining of vulcanized rubber containing age resisters, the sheets were exposed to the light of a double open-arc series connected at a distance of 75 cm. The electrodes used were Eveready Sunshine Carbons. The arc was operated at 220 volts and 30 amperes. The discoloration in such a test closely corresponds to that caused by direct sunlight.

Into 163.5 parts of the following white master batch was milled 0.5 part of the material under test. These stocks were then press-cured in clean molds for 60 minutes at 126° C. Since a small amount of color comes from the accelerator, a control (Table II) was used to avoid any error in comparing the effects of the age resisters. The master batch was as follows (in parts by weight):

Pale crepe	100.00	Sulfur	2.75
Titanox B[a]	20.00	Heptaldehyde aniline[b]	0.25
Lithopone	20.00	Stearic acid	0.50
Zinc oxide	20.00		163.50

[a] A trade-marked white pigment composed of 25% titanium dioxide and 75% precipitated barium sulfate.

[b] Reaction product of heptaldehyde with the Schiff base formed by the reaction between heptaldehyde and aniline and known to the trade as Heptene base.

Comparative results of these tests are given in Table II. Variations in order of merit before exposure were difficult to classify.

Correlation of Constitution with Aging and Staining

4-Hydroxy-*N*-phenyl morpholine (compound *E*, Table I) imparts very good aging characteristics to rubber, approximately as good as the widely used phenyl-β-naphthylamine. It is better in this respect than 2-methyl-4-hydroxy-*N*-phenyl morpholine (compound *F*). From Table II it appears that the introduction of the methyl group into the 2-position in compound *E* has reduced the staining characteristics, whereas the methyl group in the 3-position greatly increased the staining.

It would seem that there is more staining when the 3-position is filled; for example, compounds *D*, *G*, and *H* graded as 5, 6, and 7 after exposure. Apparently in the substituted phenyl morpholines, phenyl in the 3-position causes most staining.

In so far as can be determined from the limited data available, the effect of position of substituents in the benzene ring is, from least to most, as follows: 2,4 <4 <2 <3 <3,4.

TABLE II. RESULTS OF STAINING TESTS

		Order of Merit, Best to Least	
		Before exposure to arc	After exposure to arc
A.	Control	1	1[a]
B.	Phenyl-β-naphthylamine	8	8
C.	2-Hydroxy-*N*-phenyl morpholine	3	4
D.	3-Hydroxy-*N*-phenyl morpholine	4	5
E.	4-Hydroxy-*N*-phenyl morpholine	2	3
F.	4-Hydroxy-2-methyl-*N*-phenyl morpholine	5	2
G.	4-Hydroxy-3-methyl-*N*-phenyl morpholine	6	6
H.	4-Hydroxy-3-phenyl-*N*-phenyl morpholine	7	7

[a] Variations in shade more noticeable, although not marked from 1 to 6 with 7 worse and 8 very dark.

TABLE I. TESTS ON ARTIFICIALLY AGED RUBBER STOCKS[a]

		M. P.	Test	Tensile Strength Kg./sq. cm.	Tensile Strength Lb./sq. in.	Elongation at Break
		° *C*.				%
A.	Control	...	Original	253.9	3610	675
			After 7 days in Geer oven	157.2	2240	485
			After 2 days in Bierer bomb	67.5	960	320
B.	Phenyl-β-naphthylamine	...	Original	242.8	3450	690
			After 7 days in Geer oven	202.2	2880	595
			After 2 days in Bierer bomb	198.6	2825	600
C.	2-Hydroxy-*N*-phenyl morpholine	128	Original	265.8	3780	670
			After 7 days in Geer oven	145.4	2070	460
			After 2 days in Bierer bomb	103.9	1450	492
D.	3-Hydroxy-*N*-phenyl morpholine	124.5	Original	255.0	3630	665
			After 7 days in Geer oven	163.8	2330	505
			After 2 days in Bierer bomb	91.9	1310	488
E.	4-Hydroxy-*N*-phenyl morpholine	174	Original	243.2	3460	690
			After 7 days in Geer oven	200.5	2860	595
			After 2 days in Bierer bomb	198.2	2820	600
F.	4-Hydroxy-2-methyl-*N*-phenyl morpholine	133	Original	236.0	3360	635
			After 7 days in Geer oven	156.0	2220	495
			After 2 days in Bierer bomb	77.9	1110	417
G.	4-Hydroxy-3-methyl-*N*-phenyl morpholine	114	Original	255.0	3630	675
			After 7 days in Geer oven	196.0	2790	525
			After 2 days in Bierer bomb	146.2	2076	557
H.	4-Hydroxy-3-phenyl-*N*-phenyl morpholine	146	Original	255.8	3636	625
			After 7 days in Geer oven	163.8	2328	480
			After 2 days in Bierer bomb	127.2	1801	520

[a] Cured in press 45 minutes at 143.9° C.; sheets 15.24 cm. × 20.32 cm. × 2.4 mm.

Correlation of Solubility in Rubber and Molecular Weight

The authors carried out a series of tests on three of these compounds and determined approximately the solubility limits in a lightly loaded stock. A base stock was designed which cured in 60 minutes at 143° C. without sulfur bloom, according to the following recipe; after long storage in cloth no sulfur bloom appeared on the control:

Pale crepe rubber	100.00
Zinc oxide	10.00
Sulfur	2.50
Thermax (*4*)[a]	5.00
Butyraldehyde aniline accelerator[b]	0.50
	118.00

[a] Trade-marked name for a carbon black made by the thermal decomposition of undiluted natural gas in a furnace specially designed for that purpose.

[b] Reaction product of butyraldehyde with the Schiff base formed from aniline and butyraldehyde.

TABLE III. EFFECT OF MOLECULAR WEIGHT

Age Resister	Mol. Wt.	Part Age Resister per 100 Parts Rubber	Surface Appearance after 2-Weeks Storage
Control	...	0	No bloom
4-Hydroxy-*N*-phenyl morpholine	179	0.2	No bloom
		0.4 or more	Bloom
4-Hydroxy-3-methyl-*N*-phenyl morpholine	193	0.2	No bloom
		0.4	No bloom
		0.6 or more	Bloom
4-Hydroxy-3-phenyl-*N*-phenyl morpholine	255	0.2	No bloom
		0.4	Faint bloom
		0.6 or more	Bloom

The age resisters were added in concentrations shown in Table III, and the sheets were cured 60 minutes at 143° C.

Substitution of a hydrocarbon radical, such as methyl, into the aryl nucleus increases the solubility of the 4-hydroxy-*N*-phenyl morpholine in the base stock used. If the methyl group is replaced by a phenyl group, the solubility is slightly decreased.

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