Patented Jan. 27, 1953

2,626,887

UNITED STATES PATENT OFFICE

2,626,887

RAYON TIRE CORD AND METHOD OF MAKING SAME

Joseph C. Ambelang, Akron, Ohio, assignor to The Firestone Tire & Rubber Company, Akron, Ohio, a corporation of Ohio

No Drawing. Application May 3, 1949, Serial No. 91,219

8 Claims. (Cl. 154—136)

This invention relates to the manufacture of rayon filaments, and it relates especially to superior rayon cord or fabric for reinforcing rubber, synthetic rubber and plastic articles.

In the commercial production of rayon filaments it is considered necessary to apply a finish to the rayon yarn prior to twisting it into a thread or cord. The finish is usually applied as a dilute water solution or dispersion to the wet yarn soon after it is formed and washed. After the treated yarn is dried, it is ready for the twisting operations.

Rayon finishes generally include a lubricating wax or oil to improve the mechanical processing of the yarn in the twisting machines. Many of the finishes heretofore commercially employed have seriously interfered with adhering rayon cord or fabric to rubber, as in a pneumatic tire, fan belt or reinforced hose.

It is therefore an object of this invention to provide an improved rayon finish, the use of which will result in satisfactory processing in the twisting operations without interfering with subsequent adhesions of the rayon cord or fabric to a rubber or plastic material. Another object is to provide an improved rayon tire cord and method of manufacturing same. The above and further objects will be apparent in the description of the invention, which follows.

The objects of the invention are realized by a rayon finish consisting essentially of (1) a water insoluble lubricant, (2) a liquid or solid polyalkene oxide and (3) an alkali metal alkarylsulfonate, dispersed in water. The novel finish has been found (*a*) to function satisfactorily in the rayon mill permitting the yarn to be handled and twisted without appreciable breakage of the filaments, (*b*) to result in higher adhesion of rubber to rayon than has been obtained with conventional oil and wax finishes and (*c*) to produce a rayon tire cord of improved fatigue life over rayons with conventional oil and wax finishes.

The water insoluble lubricant may be any of a number of conventional rayon lubricants, including paraffins and esters such as butyl palmitate and methyl oleate. A preferred lubricant is a mineral oil, which may, for example, range in viscosity from ordinary medicinal heavy mineral oil to a low viscosity, "light" mineral oil.

The polyalkene oxides, sometimes called polyalkene glycols or polyoxyalkene glycols, are preferably liquid or solid, water soluble polyethene oxides or polypropene oxides, the molecular weights of which may vary from about 1000 to

10,000 or higher. Polyalkene oxides of various molecular weights are commercially available. For example, "Carbowax," a series of polyethene oxides, is available from the Carbide and Carbon Chemicals Corp.; each variety of Carbowax carries a numerical designation of the approximate molecular weight thereof. Likewise, the polypropene oxides are available from the same supplier under the name "Ucon."

The alkali metal alkarylsulfonates are necessary to disperse the lubricant in the water of the finish. These sulfonates have been found by the inventor not to interfere with adhesion of rayon to rubber when employed in the rayon finish, and in some cases to improve the adhesion, whereas many commercial wetting or dispersing agents tend to reduce the adhesion of rayon to rubber. Examples of the alkarylsulfonates include the various sulfonated alkylbenzenes, such as dodecylbenzenesulfonate, decylbenzenesulfonate, etc.; the various sulfonated alkylnaphthalenes, such as dibutylnaphthalenesulfonates, triamylnaphthalenesulfonates, mono and dinonylnaphthalenesulfonates, etc.; sulfonated bis (alkylbenzene) alkanes, such as bis (amylbenzene) ethanesulfonate, bis (dodecylbenzene) ethanesulfonate and condensation products of alkylbenzenes with aldehyde potassium sulfonates; the various alkylbiphenylsulfonates, such as diamylbiphenylsulfonates; and other known alkarylsulfonates.

The finish is made up to contain about 0.25% to about 2% of non-aqueous ingredients, and usually contains 0.4% *to* 1.0%. The dried rayon yarn gains about 0.4% to 1.0% in weight due to the finish. The lubricant and polyalkene oxide are usually employed in approximately equal proportions, although this proportion does not appear to be critical, so long as each is present in appreciable proportions in the finish. The proportion of the alkali metal alkarylsulfonate employed varies somewhat as to the dispersing power of the particular sulfonate used, the proportion and character of the lubricant, and the proportion of water in the finish.

Many finishes have been made in accordance with the invention and applied to rayon yarn in the laboratory. After the yarns were formed into tire cords, they uniformly displayed better resistance to deterioration upon aging and better adhesion to rubber than conventionally finished rayon tire cords. These and other finishes of the invention have been found to improve the rubber to rayon adhesion by a cellophane film adhesion test described below.

CELLOPHANE FILM ADHESION TEST

Plain transparent cellophane (that is, without wax or lacquer coating), of 0.0016 gauge or greater, is cut into 6 by 12 inch strips. The strips are immersed in an aqueous dispersion of the finish to be tested, usually 0.5 to 1.0%, and then dried in air, about two hours being required. The strips are then run quickly through a standard tire cord dip, such as natural latex containing casein (made soluble with sodium hydroxide) and again dried in air, overnight. The dried film is next laid transversely between plies of a standard rubber tire body ("skim") stock in an adhesion pad built up as follows:

1. Skim stock (0.200 gauge).
2. Tire cord fabric frictioned twice, skimmed once to 0.060 gauge.
3. Skim stock (0.025 gauge).
4. Cellophane test film.
5. Skim stock (0.025 gauge).

The cellophane is stitched and rolled to remove wrinkles and bubbles. The pad is cured in a mold 60 minutes at 280° F. to produce a cured pad 8 by 5 inches by 0.25 inch.

The cured pad is cut lengthwise into one inch strips, and one end of each strip is cut so that ply number 5 may be pulled away from the cellophane. The loose end of ply 5 is fastened in the lower clamp of a Scott tensile machine, model L–6, and the force is measured sufficient to separate the rubber from the cellophane at a rate of one inch per minute.

The upper limit of adhesion thus measurable is 11–12 pounds, above which the cellophane film breaks so that an even rate of separation is impossible.

With each series of tests a blank is run, the blank being cellophane dipped in water without added finish. Each finish is rated by means of an adhesion index.

$$\text{Adhesion index} = \frac{\text{Separating force for finish}}{\text{Separating force for blank}}$$

The adhesion between rubber (dip and skim stock), and the regenerated cellulose surface is represented by an adhesion index of 1.00. Finishes which improve adhesion will raise the index above 1.00, whereas finishes which reduce adhesion will lower the index below 1.00.

The adhesion index of a given finish appears to be a satisfactorily duplicable figure, even though the actual adhesive force varies more widely. This variation may be attributed to variations in the cellophane or experimental conditions. The following data illustrates the range of values obtained by means of the cellophane adhesion test:

Table I

Finish	Separating Force in lbs./in. (average of 2 strips)		Adhesion Index
	Test	Blank	
Conventional finish including sorbitan palmitate	0.34	1.58	0.22
	0.49	1.83	0.27
Combination of mineral oil, a polyalkene oxide (Polyglycol P 1200 from Dow Chemical Co.) and sodium dinonylnaphthalenesulfonate	1.96	1.58	1.24
	1.52	1.30	1.17

Another test employed in evaluating the finish of the invention is the following:

HEAT AGING TEST

Samples consisting of 2.5 grams of rayon tire cord containing the finish under test are reeled to skeins, dried, and then permitted to absorb moisture until they are in equilibrium with an atmosphere of 55% relative humidity, 75° F. The skeins are then inserted into Pyrex glass tubes, 75 mm. in diameter and 12 inches long, closed at one end. The skeins are moved to the closed end of the tube by shaking or whirling thereof, care being taken to handle the skeins as little as possible to prevent their absorbing perspiration from the hands. The tubes are then sealed at a 9 inch length.

The samples are heated for 6 hours at a temperature of 150° C.±1° C. An oil bath is desirable for this heating treatment, but an oven with uniform heat distribution may be used if a suitable oil bath is not available.

At the end of the heating period the tubes are removed from the source of heat, allowed to cool and then opened, care being taken to avoid injuring the cord by broken glass. After the samples have been removed from the tubes the cords are dried at 110° C. for 4 hours and then broken on a Scott X–3 cord tester.

Results are expressed as per cent heat aging loss, obtained by subtracting the strength after aging from the strength before aging, and dividing by the strength before aging.

The following examples are given to show both laboratory and production tests on some preferred finishes of the invention.

Example 1

The following finish was prepared:

	Parts by weight
Mineral oil	0.25
Carbowax 1500	0.20
Condensation product of amylbenzene and acetaldehyde potassium disulfonate (General Chemical 1–3335–6)	0.05
Water	99.50

An adhesion index of 1.20 was obtained on the above finish by the cellophane film test (supra). This finish was then applied to rayon yarn at a rayon plant in a continuous production run in comparison with a conventional finish comprising 0.5% of sorbitan palmitate as a control. The rayon was continuously produced as 1100/2 construction yarn with a slight twist. Processing characteristics of the finish and tensile data, both normal and aged (latter obtained in accordance with the above-described heat aging test) are as follows:

Finish	Spinning Appearance of Yarn	Twisting	Breaking Load in lbs.		Heat Aging Loss
			Normal	Aged	
					Percent
Example 1	Good	Satisfactory	17.69	11.5	35
Control	Excellent	do	18.95	10.7	43.5

Example 2

The following finish was prepared:

	Parts by weight
Mineral oil	0.25
Carbowax 4000	0.25
Sodium dinonylnaphthalenesulfonate	0.10
Water	99.40

An adhesion index of 2.67 was obtained on the above finish by the cellophane film test. This finish was then applied to continuous production 1100/2 rayon yarn as in Example 1, and the following data were obtained:

Finish	Spinning Appearance of Yarn	Twisting	Breaking Load in lbs.		Heat Aging Loss
			Normal	Aged	
					Percent
Example 2	Excellent	Satisfactory	16.6	10.6	36
Control	do	do	18.4	8.4	53

Example 3

The finish of Example 2 was used in making 1100/2 rayon tire cord for a flexing test on the United States Flexing Machine in comparison with a similar control cord having a conventional sorbitan palmitate finish. The test pads, containing 28 cords vulcanized in rubber, were flexed until several cords had separated from the rubber. The test data are as follows:

	Finish	
	Control	Example 3
Flexes	3,276	4,256
Separated cords	28	11
Rating	3	1

The above test shows that the control cords all separated after 3276 flexes, whereas only 11 cords finished in accordance with the invention had separated after 4256 flexes. The rating means that the cord finished per Example 3 was much better than the control.

Example 4

The following finish was prepared:

	Parts by weight
Medicinal mineral oil	0.33
Carbowax 1500	0.33
Sodium dinonylnaphthalenesulfonate	0.14
Polyvinyl alcohol (medium viscosity)	0.20
Water	99.00

An adhesion index of 2.45 was obtained on the above finish by the cellophane film test. This finish was then applied in a production run in a rayon plant for the continuous production of 2200/2 rayon tire cord. The rayon yarn in this instance was produced with no twist prior to the application of the finish. A 2200/2 rayon tire cord from the regular commercial production of this manufacturer was then used in determining the static and flexed adhesion to rubber. The static test is described in a publication of Lyons, Nelson and Conrad, Research Report AIC-99 of the U. S. Department of Agriculture, Southern Regional Research Laboratory, New Orleans 19, Louisiana, dated October 1945. The flexed test is run by first curing 5 cords in a rubber pad, from one end of which the cords extend, and flexing the pad under a load of 5 pounds for 10 hours. Thereafter, the pad is died to produce the required test specimen and the tensile measurement is carried out by means of a Scott X-3 machine or a Suter machine, as described in the

Lyons et al. publication. The following data were obtained:

Finish	Adhesive Force in lb./in.	
	Static	Flexed
Example 4	43.6	33.5
Control	35.6	24.1

The above test shows that the invention results in much higher rubber-to-rayon adhesions.

What is claimed is:

1. Rayon tire cord comprising rayon filaments carrying on the surface thereof 0.4 to 1.0% by weight of a finish consisting of approximately equal parts of a mineral oil and a polyalkene oxide having a molecular weight between 1000 and 10,000 together with a relatively small proportion of an alkali metal alkarylsulfonate containing at least 8 alkyl carbon atoms in the molecule.

2. Rayon tire cord as in claim 1, the polyalkene oxide being polyethene oxide.

3. Rayon tire cord as in claim 1, the alkarylsulfonate being dinonylnaphthalenesulfonate.

4. Rayon tire cord as in claim 1, the alkarylsulfonate being the condensation product of amylbenzene and acetaldehyde potassium disulfonate.

5. Rayon tire cord as in claim 1, the alkarylsulfonate being triamylnaphthalenesulfonate.

6. Method of making rubber-reinforcing rayon filament, comprising applying to freshly formed rayon filament a dilute aqueous dispersion containing 0.4 to 1.0% by weight of a finish consisting of approximately equal parts of a mineral oil and a polyalkene oxide having a molecular weight between 1000 and 10,000 together with a relatively small proportion of an alkali metal alkarylsulfonate containing at least 8 alkyl carbon atoms in the molecule.

7. Method of making a reinforced rubber article, comprising applying to a cellulose reinforcing member 0.4 to 1.0% by weight of the member of a finish by treating the member with a water dispersion containing 0.4 to 1.0% by weight of the dispersion of approximately equal parts of a mineral oil and polyalkene oxide having a molecular weight between 1000 and 10,000 together with a relatively small proportion of an alkali metal alkarylsulfonate containing at least 8 alkyl carbon atoms in the molecule, then applying to the surface of said member a natural latex adhesive containing casein, drying the so-treated member, and then vulcanizing rubber composition in contact with the dried member.

8. Vulcanized reinforced rubber article comprising a cellulose reinforcing member adhered to vulcanized rubber by means of a natural latex adhesive containing casein, said member carrying on its surface 0.4 to 1.0% by weight of the member of a finish composition consisting of approximately equal parts of a mineral oil and a polyalkene oxide having a molecular weight between 1000 and 10,000 together with a relatively small proportion of an alkali metal alkarylsulfonate containing at least 8 alkyl carbon atoms in the molecule.

JOSEPH C. AMBELANG.

(References on following page)

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,149,498	Bludworth	Mar. 7, 1939
2,211,960	Meigs	Aug. 20, 1940
2,211,964	Tanberg	Aug. 20, 1940
2,300,074	Strain	Oct. 27, 1942
2,385,110	Seymour et al.	Sept. 18, 1945
2,393,863	Myers	Jan. 29, 1946
2,418,752	Brown	Apr. 8, 1947
2,497,536	Chandler	Feb. 14, 1950
2,511,629	Entwistle	June 13, 1950

OTHER REFERENCES

"Carbowax Compounds and Polyethylene Glycols," by Carbide and Chem. Corp., copyrighted on June 30, 1946.