

1

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OILS FOR HEAT TREATMENT OF THERMOPLASTIC FIBERS

Yasuharu Kato, 1-11 Maruyama-cho, Gamagori, Aichi-Prefecture, Japan, and Hirokazu Matsueda, 350 Azuma-cho, Toyohashi, Aichi-Prefecture, Japan

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2 Claims

ABSTRACT OF THE DISCLOSURE

In the working and thermal treating of synthetic thermoplastic polymer fibers, improved lubricating compositions are provided comprising at least one lubricating compound of the group tri-2-ethylhexyltrimellitate, triisodecyltrimellitate, tri-polyoxyethylene lauryltrimellitate, tetra-isodecylpyromellitate, and tetra-octylmethylene-bis-phthalate, which may be combined with conventional materials employed in such compositions.

This invention relates to the oils for heat treatment of thermoplastic fibres.

The fabrication of synthetic fibres consists of many processes such as spinning, stretching, twisting, weaving, knitting and bulking etc., and in each of these processes, various treating oils are used according to the particular purpose.

Especially in the fabricating processes of thermoplastic fibres, certain heat treatments are applied in order to improve in their quality. Hitherto, in order to attain smooth heat treatment, treating oils having little change of such quality as smoking, evaporating, tarring, decomposing, etc., are usually required.

It is considered to be the important factor which is desired of the treating oils used for heat treatment of fibres, to preserve the lubricating, bundling and antistatic properties of fibres which properties are lost by the effect of change of such quality as smoking, evaporating, tarring, decomposing of the treating oils. Up to now, from this viewpoint, various lubricating oils, antistatic agents and emulsifiers having good heat resisting property were selected and some appropriate combinations of such agents were actually been in use. However, further improvement of their natures are still required at present.

The inventors, for the purpose of improving the heat treatment of synthetic fibres, have investigated the heat resisting property of every component of the treating oils on the basis of the said viewpoints. However, the inventors have found that, satisfactory effect of treatment can not always be obtained, even when the oils used, showing little change of such quality as smoking, evaporating, tarring, decomposing, during the heat treatment of fibres. On the contrary, the inventors have found that some of them may adversely affect with the quality of the fibre through the heat treatment. An example of such worse effect by the treating oil upon the fibre shows a phenomena that the sufficient strength of the yarn can not be obtained, by the stretch of yarn of ordinary stretching ratio, and another showing that, the strength of yarn is remarkably lowered when a certain heat treatment is applied to the stretched yarn.

It is usually the basic idea to formulate oils for the fibre treatment, in the past, that, in consideration of lubrication between fibre-fibre and between fibre-metal, at first, an appropriate lubricant is selected accordingly to each treatment, secondly, an emulsifier, which is required to emulsify and disperse the lubricant into water, is selected then, each lubricant and the emulsifier in the necessary but smallest quantity, are mixed, an antistatic

2

agent also added, if necessary, and finally, the whole mixture being prepared as the product of high concentrated liquid or that of stable paste.

As mentioned above, when the oil for heat treatment of fibre is prepared by mixing lubricant, emulsifier and antistatic agent, the nature of the oil is, in most cases characterized by the lubricant contained as the main component in the mixture.

In the past, the materials known as the lubricant of the heat treatment of fibre, there are such higher alcohol esters of higher fatty acids as mineral oils, neutral fats and natural oil of spermwhale, and such lower alcohol esters of higher fatty acids as methyl and butyl stearate. These materials have good lubricating property. Most of them may be used in many application fields, while showing the phenomena of evaporating, smoking, staining and tarring in the case of heat treatment. Such phenomena may induce the change of the quality of the lubricants which in many case, results in obstructing smooth heat treating process.

As lubricants having good heat resistance for heat treating oils of fibres, there have already been prepared, such dibasic fatty acid esters as bis-2-ethylhexylsebacate (Publication No. 1964/16,160; E.P. No. 95,004) and such aromatic carboxylic esters as benzoic acid esters with the alcohol reduced from the coconut oil and dioleil phthalate (Publication No. 1966/16133). These lubricants may be the lubricants having good heat resistant property against evaporation, smoking, tarring, staining, etc., however, they remarkably affect, as aforementioned, the quality of the fibre through the heat treatment and it is not desirable to produce high quality fibres. Especially, in the case to produce polyamid fibre yarn, and polyester fibre yarn having high strength, to be used for fire cords, the oils consisting of aforementioned lubricating components, may lead to lower the strength of fibre yarn during the process of the heat treatment. Moreover, the desired strength of fibre yarn may not be obtained, even if certain appropriate conditions are adopted in the process of thermal stretching of fibres, and in some case may cause a trouble of melting fibres during the stretching process.

The mechanism of treating oils acting on fibre has not been cleared, but it may be considered that the lubricant, the main component in the treating oil, penetrates into the fibre, during the process of heat treatment, and affecting the orientation of polymer molecules of fibre, or that, the radicals produced, by thermal or oxygenic decomposition of treating oil, change into polymer molecules, and thus causing the cut-off of the polymer molecules.

In consideration of the above mentioned fact, the inventors studied to prepare such treating oils that have excellent heat resisting property and give no adverse effect on the fibre's nature through the heat treatment, and as the result, have found out that aromatic polycarboxylic esters with specific chemical constitutions especially have the excellent properties as lubricants.

The object of this invention is to improve the aforementioned defects and to produce new excellent treating oils for the heat treatment of thermoplastic fibres. Then another object of this invention is to produce oils with excellent heat resisting property, which show little change of property such as evaporation, smoking, tarring, staining, etc. through the heat treatment process of thermoplastic fibres.

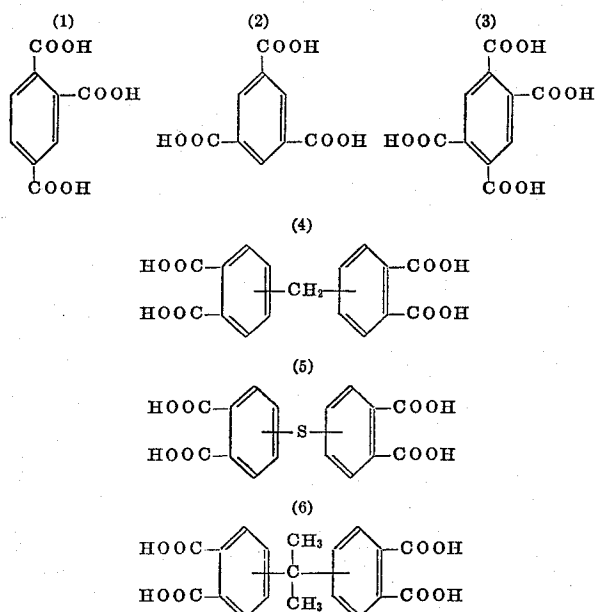
In addition, another object of this invention is to produce treating oils having the ability to reduce deterioration of thermoplastic fibres by heat treatment.

This invention aims to complete the above mentioned objects. In summary, the invention relates to the oils used for the heat treatment of the thermoplastic fibres, charac-

3

terised by mixing such lubricant as triesters and tetraesters of aromatic polycarboxylic acid, in which a single aromatic nucleus, has more than a single carboxyl group and as a whole having more than three carboxyl groups in a single molecule.

There are following aromatic carboxylic acids as the basic materials to derive the aromatic polycarboxylic esters: examples having a single aromatic nucleus in a single molecule are (1) 1,2,4-tri-carboxybenzene (trimellitic acid), (2) 1,3,5-tri-carboxybenzene (tri-mesic acid), (3) 1,2,4,5-tetra-carboxybenzene (pyromellitic acid), etc., and examples having two aromatic nuclei in a single molecule of aromatic polycarboxylic acids are (4) condensed product of two molecules of phthalic acids by a methylene group, (5) condensed product of two phthalic acids by a thioether group, (6) condensed product of two phthalic acids by a propylidene group, etc. The chemical constitution of these substances are shown as follows:



As the substances with hydroxyl groups, producing esters by combining with aromatic polycarboxylic acids, there are alcohols having carbon atoms of 1 to 18, or their alkylene oxides additives, represented by their ethylene oxides, propylene oxides, etc. and the above mentioned alkylene oxide additives of alkylphenols having carbon atoms of 4 to 12, can be applied. Furthermore, in the alcohols having carbon atoms of 1 to 18, there include saturated and unsaturated alcohols with linear chain or side chain.

All carboxylic groups in aromatic polycarboxylic acids may be esterificated with the same substance with the hydroxyl groups and different substances with hydroxyl groups.

The condition for selection of substances with hydroxyl group, to attain the purpose of this invention, requires that the number of the total carbon atoms of the compound with hydroxyl groups combining with carboxyl groups should be amounted to 24, to form aromatic polycarboxylic esters. Also, when alkylene oxide additives of alcohols and alkylphenols are used, as compounds with hydroxyl groups, the amount of alkyleneoxide additives should be less than 10 mols, and the amount of above 10 mols, it is not preferable, in order to achieve the object of this invention.

The reasons are as follows: firstly, as the length of chain of the alkylene oxides increases, the thermal decomposition and oxygenic decomposition of polyalkylene oxide groups predominantly progress by heat treatment, which resulting in undesirably lowering the heat resist-

4

ance, and secondly, the viscosity increases, as the molecular weight of aromatic polycarboxylic esters increases, which resulting in losing appropriateness of the material as the lubricants.

This invention is to offer the heat treating oils, by mixing triesters or tetraesters of aromatic polycarboxylic acids as the essential components, and there is no restriction of the amount of mixing ratio. Generally the amount of the essential component may be 30-90%, in order to bring about the effect of this invention, and preferably, it is 50-80%.

In this invention, as the components other than the important ones, the known surface active substances can be freely selected to improve emulsifying and stabilizing properties, antistatic property and bundling property. Also, so far as the effect of this invention may not be lost, the known lubricants may be used together with the claimed effective components.

For example, the result of the comparison test of heat resistant properties between the aromatic polycarboxylic esters used as the lubricants in this invention and ordinary lubricants often used so far are shown as follows:

25	Lubricants	Heat resistance Test 1		Heat resistance Test 2, time to tarring (min.)
		Heating loss (percent)	Tarring	
Substances in this invention:				
30	Tri-2-ethylhexyltrimellitate.....	0.9	—	150
	Tri-isodecyltrimellitate.....	0.8	—	>200
	Tri-POE(3)lauryltrimellitate.....	1.5	—	120
	Tetra-isodecylpyromellitate.....	0.5	—	>200
	Tetra-octylmethylen- bisphthalate.....	0.4	—	>200
Known substances:				
35	Di-2-ethylhexylsebacate.....	6.5	±~	(1)
	Di-oleylphthalate.....	1.7	+	60
	Oleylaurate.....	2.1	+	45

¹ Almost no tarring evaporated.

TEST METHOD

Heat resistance test 1

10 ml. of the sample is weighed and put into the weighing glass bottle with inside diameter of 50 mm. and depth of 75 mm. The sample is heated in the dryer with air circulator at $200 \pm 5^\circ \text{C}$. for 3 hours. The ratio of weight loss by heating was determined. At the same time, tarr-like substance deposited and adhered to the inside surface of the bottle after heat treatment was observed by the naked eye. The results are shown on the basis of the following criteria.

Tarring:

- no tarring was observed
- ± hardly observed
- + tarr observed
- ++ tarring was remarkable

Heat resistance test 2

The stainless steel plate with thickness of 10 mm., diameter of 16 mm., and the concave part of 5 mm. depth is used. The sample is put into this concave part so that the sample thickness may become 1 mm. thickness at the deepest part of the concave. Then, the stainless steel plate is heated and maintained at 240°C . of the surface of the plate.

Evaluation of heat resistance took place to determine the time when the surface temperature of the stainless steel arrived at 240°C . until the sample has completely become tar.

EXAMPLE 1 (TREATING OIL A)

	Percent
Tri-isodecyltrimellitate	65
POE (12 mols) glycerine mono disesquiolate	15
POE (6 mols) nonylphenylether	15
Na sulfonate of refined petroleum oil	5

5

EXAMPLE 2 (TREATING OIL B)

	Percent
Trioleyltrimellitate	50
Glycerine monoacetodiolein	20
Polyoxyethylene derived from castor oil	12
POE (5 mols) nonylphenylether	8
Na sulfonate of refined petroleum oil	5
Ka salt of laurylphosphate	5

Polyethyleneterephthalate with the critical viscosity 0.85 in the orthochlorophenol solution at 25° C. is used to melt and spin fibres in the ordinary method. Then, by lubricating with 15% emulsion of the treating oil consisting of the above Example 1 and Example 2, non-stretched polyethyleneterephthalate fibre of 1500 denier 48 filament is obtained.

In succession to the above, this non-stretched fibre is thermally stretched in the ratio of 6.5 times by the second step of stretching (the first stretching at 90° C., the second stretching at 200° C.). Furthermore, the heat treatment is applied at 150° C., and the stretched yarn of 250 denier 48 filament is obtained. Table 1 shows the heat resistance of treating oils in the stretching process and the strength of the yarn obtained, compared with that of the known treating oils.

TABLE 1

	Heat resistance at stretching process	Strength of stretched thread, g/d.
Treating oil:		
A.....	Smoking, almost no tarring.....	9.4
B.....	do.....	9.5
Known treating oil:		
1.....	Smoking predominantly, tarrying is observed a little.....	8.3
-2.....	Smoking, tarrying hardly observed.....	8.9

In the above table, the composition of the known treating oils are as follows.

THE KNOWN TREATING OIL 1

	Percent
Di-2-ethylhexylsebacate	40
Mineral oil (viscosity at 30° C., Redwood 200 sec.) ..	25
Polyoxyethylene derived from castor oil	15
POE (5 mols) oleylether	15
Na sulfonate of refined petroleum oil	5

THE KNOWN TREATING OIL 2

	Percent
Di-oleylphthalate	65
POE (12 mols) glycerine mono-di-sesquiolate	15
POE (4 mols) nonylphenylether	15
K-salt of POE (3 mols) laurylphosphate	5

EXAMPLE 3 (TREATING OIL C)

	Percent
Tri-isodecyltrimellitate	70
Polyoxyethylene derived from castor oil	13
POE-dodecylphenylether	17

EXAMPLE 4 (TREATING OIL D)

	Percent
Tetra-octylmethylene-bisphthalate	45
Mineral oil (viscosity at 30° C., Redwood 350 sec.) ..	20
Polyoxyethylene derived from castor oil	10
POE nonylphenylether	20
Na salt of laurylsulfonate	5

EXAMPLE 5 (TREATING OIL E)

	Percent
Tri-POE (3 mols) lauryltrimellitate	65
POE-nonylphenylether	27
Na sulfonate of refined petroleum oil	5
K salt of POE laurylphosphate	3

The non-oiled yarn is prepared by removing the oil from the stretched yarn (250 denier 48 filament) of polyethyleneterephthalate obtained by using the treating

6

oil A of the Example 1. This yarn is oiled with 10% emulsion of the treating oil consisting of the above Examples 3, 4 and 5. The oiled yarn, after being dried in the hot air dryer at 80° C. for one hour, further treated at 200° C. for two hours. After the heat treatment the strength of the yarn was determined. Then, the ratio of remaining strength of the oiled yarn was calculated against the strength of the non-oiled yarn before heating.

The Table 2 shows the results in comparison with the known treating oils.

TABLE 2

	Quantity of adhere (percent)	Rate of remaining strength (percent)
Treating oil		
15 Non-oiled yarn.....		98.3
Treating oil:		
C.....	0.95	97.0
D.....	0.87	95.5
E.....	1.03	96.2
20 Known treating oil.....	0.92	84.8

In the above table, the known treating oil means the following composition.

	Percent
Glycerine-mono-acetodiolein	30
25 Mineral oil (viscosity 30° C. Redwood 130 sec.)	30
POE sorbitan-triolate	15
POE-triethanolamino stearate	15
Na sulfonate of refined petroleum oil	10

The non-stretched yarn of polyethyleneterephthalate is oiled with the emulsion of the treating oils C, D and E, shown in the Examples 3, 4 and 5. Then, it was thermally stretched.

The yarn treated by the known treating oils are apt to smoke on the heater plate during the stretching process, staining the heating plate and necessitating the cleaning of the plate many times. In contrast with this, the yarn treated by the treating oils C, D and E of this invention, all of them show no smoking and observed almost no staining of the heating plate. The known treating oil here, is the same as shown below in Table 2.

EXAMPLE 6 (TREATING OIL F)

	Percent
Trioctyltrimellitate	40
45 Dioctylsebacate	25
Na salt of laurylsulfonate	10
Polyethylenglycol-palmitate	12
POE-nonylphenylether	13

The melted and spinned, non-stretched 6 nylon fibre, was oiled with 15% emulsion of treating oil F, consisting of the above composition. Then, it was stretched to obtain nylon fibre of 100 denier 24 filament.

Following this, the material was provisionally thrown continuously for 30 days. The fibre treated by the known treating oil, it smokes largely, and was so stained as to need cleaning only at tenth day of continuous throwing.

In the contrast with this, the fibre treated by the treating oil F of this invention, smokes very little, and no cleaning was needed after 30 days' continuous working.

The known treating oil consists of the following composition:

	Percent
Oleylaurate	30
Mineral oil	35
K salt of laurylphosphate	10
65 POE-oleylether	15

What is claimed is:

1. In the process for the heat treatment of synthetic thermoplastic polymer fibers wherein a lubricating composition is applied to the fibers prior to the heat treatment step, the improvement comprising applying to said fibers as the lubricating composition, a composition consisting essentially of a lubricant emulsified in water, and one or more emulsifying agents, said lubricant being selected

7

from the group consisting of esters of alcohols and polycarboxylic acids, said alcohol member selected from the group consisting of alkanols containing 1 to 18 carbon atoms and condensation products of an hydroxy compound selected from the group consisting of said alkanols and alkyl phenols wherein the alkyl group contains 4 to 12 carbon atoms with less than 10 mols per mol of said hydroxy compound of an alkylene oxide selected from the group consisting of ethylene and propylene oxide; and said polycarboxylic acid member selected from the group consisting of trimellitic acid, tri-mesic acid, pyromellitic acid, methylene-bis-phthalic acid, thio-bis-phthalic acid and 2-propylidene-bis-phthalic acid.

2. The process of claim 1 wherein said alcohol is selected from the group consisting of alkanols containing one to eighteen carbon atoms.

8

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10 HERBERT B. GUYNN, Primary Examiner

H. A. PITLICK, Assistant Examiner

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