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TREATING CELLULOSE DERIVATIVE MATERIALS

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This invention relates to the conditioning of textile yarns and more particularly to the conditioning of filaments and yarns composed of organic derivatives of cellulose such as cellulose acetate, cellulose propionate, cellulose acetate propionate, and cellulose acetate butyrate, to render them more amenable to textile operations such as knitting and the like. This invention also relates to compositions of matter in which cellulose derivatives such as cellulose acetate, cellulose nitrate or cellulose ethers, are combined or mixed with other substances, such as a compatible plasticizer, and a common solvent for both, with or without other useful addition agents, so that the resulting product will have properties such as will make the composition highly advantageous for use in the plastic and analogous arts, such for instance, as the manufacture of wrapping sheets, photographic film, artificial silk, varnishes or lacquers, and the like.

As is well known in the manufacture of yarns, particularly those composed of or containing cellulose organic derivatives, it is necessary to treat the yarn in order to reduce the tendency toward breakage of the individual filaments or fibers when they are subjected to various mechanical strains and to lubricate the yarn in order to facilitate handling in such operations as spinning, twisting, winding and reeling. It is also necessary to treat yarn to adapt it for use as warp or filling or for the manufacture of various types of knitted fabrics. In knitting, it is particularly important that the yarn be soft and pliable in order that it may conform readily to the contour of the needles and thus produce a closely knit fabric free from such defects as "stitch distortion," "pin holes," "laddering," and the like.

Heretofore it has been proposed to employ softening agents such as polyhydric alcohols and similar agents as ingredients of yarn conditioning or lubricating formulas, generally in connection with mineral, animal or vegetable oils. It has been found, however, that most of the known softening agents and the various formulas containing them have certain drawbacks, one of the most serious of which is high vapor pressure, and in some cases too drastic a solvent action on the yarn. Many of such agents possess slight or insufficient solvent power for the lubricants with which they are used, and it is accordingly necessary to employ blending agents or emulsifying agents in order to obtain operable yarn treating formulas. In addition, many of the known softening and lubricating agents are insufficiently soluble in water to permit satisfactory removal by aqueous scour baths.

While in the plastic and related arts cellulose acetates, nitrates and ethers have been known for decades, it has also been known that to utilize them it is necessary to mix therewith such plasticizing or conditioning agents as camphor, castor oil, triphenyl phosphate, monochlornaphthalene or the like. Certain of these and other addition agents are also added for the purpose of reducing the inflammability of the product. Plastic inducing agents, such as the higher alcohols and their esters, are sometimes also added. Similarly, addition compounds of various kinds have been employed to increase flexibility, transparency, toughness, and other properties which will enhance the value of the resulting product. Addition products for the same or similar purposes are also added to cellulose acetates, nitrates and ethers to prepare them for use in the other plastic arts, such as in the manufacture of lacquers, varnishes, artificial silk filaments, moulded compounds and the like. While the plasticizers or other addition agents heretofore discovered have had their utility in the art, the increasing use to which cellulose derivatives have been put and the increasing number of desirable properties required of the cellulose derivative for most purposes has made the discovery of new and economical plasticizers or other addition agents a matter of considerable importance to the art.

This invention has as its principal object to provide an entirely new class of yarn conditioning agents which are particularly adapted for the treatment of yarns composed of or containing organic derivatives of cellulose and capable of lubricating, softening and rendering such yarns more amenable to knitting and other textile operations. A further and specific object is to provide a class of conditioning agents which augment or assist the lubricating action of various lubricants when applied to such yarns. A still further object is to provide yarn softening and lubricating formulas which can be readily removed from the yarns by the usual scour baths. A still further object is to provide an improved method for the conditioning of yarns, particularly those composed of or containing organic derivatives of cellulose such as cellulose acetate, whereby the yarn is rendered soft and pliable and capable of employment in a variety of textile operations where complicated designs or stitches are employed. Another object is to provide an improved type of yarn which is especially

amenable to textile operations including circular knitting, weaving, spinning and the like. Still another object of this invention is to produce a composition of matter which may be made into permanently transparent, strong and flexible sheets or films of desired thinness which are substantially waterproof, are unaffected by ordinary photographic fluids and possess the desired properties of a support for sensitive photographic coatings. Yet another object of our invention is to produce a composition which is capable of easy and convenient manipulation in the plastic and analogous arts, such as in the manufacture of sheets, films, artificial silk filaments, varnishes, lacquers and the like, and to produce a composition which will not injure, or be injured by, the substances or surfaces with which it is associated during manufacture. Other objects will appear hereinafter.

These objects are accomplished by the following invention which, in its broader aspects, comprises the discovery that nitroalkane and nitroalkene esters of mono- and poly-carboxylic, aliphatic, aromatic and heterocyclic acids, may be used as yarn conditioning agents and particularly as softening agents, with or without the addition of animal, mineral, or vegetable oils, in the treatment of yarns composed of or containing organic derivatives of cellulose. We have found that these compounds when employed as described in the detailed examples set forth below have a slight solvent and/or softening action on cellulose organic derivative yarns which renders such yarns soft and pliable without at the same time having too drastic an action thereon.

These compounds are prepared by esterifying the desired nitro alcohols by known methods with an organic acid having the general formula:

$$R—(COOH)_x$$

where R is an aliphatic, aromatic or heterocyclic group and x is 1 or more. By nitro alcohols we include any monohydroxy-mononitroalkane or monohydroxy-mononitroalkene.

Our invention also comprises the discovery that valuable properties may be induced in and/or contributed to compositions containing cellulose derivatives such as cellulose acetate, and synthetic polymers including polyvinyl acetals, esters, ethers, halides and the like, polystyrene, indene, coumarone and the various resins derived from acrylic acid esters, amides and the like and the various substituted acrylic acids such as methacrylic and the resins derived from glycerine, ethylene glycol and the like.

The following table includes a list of typical compounds which we have found to be useful for the purpose of our invention.

	M. P.	B. P.
Di (2-nitro-2-methylpropyl)—		
Succinate	79–80°	190–5°/1 mm.
Maleate		180–5°/1 mm.
Adipate		200–5°/1 mm.
Oxalate	90–2°	
Acetate		80–5°/1 mm.
Butyrate		90–5°/1 mm.
Phthalate	142–3°	

An example of the preparation of typical compounds of this type are as follows:

PREPARATION OF DI-(2-NITRO-2-METHYLPROPYL) PHTHALATE

A mixture of 74 parts phthalic anhydride, 120 parts 2-nitro-2-methylpropanol-1, 200 parts benzene and 5 parts conc. sulfuric acid is distilled in such a manner that the benzene is separated from the water of reaction and returned to the reaction vessel. When the required amount of water has been collected, the solution is cooled. The solid which separates is filtered and washed with sodium carbonate solution. On recrystallization from acetone, with the use of Norite, 110 parts of the ester are obtained, M. P. 142–3°.

TREATMENT OF TEXTILE YARNS

In accordance with the invention these compounds may be applied directly to the yarn during or after spinning, or may be added to the spinning solution itself. We have found that these compounds have exceptional solvent powers which enable them to dissolve mineral oils and blown and unblown, drying and semi-drying, vegetable and animal oils and accordingly they may be, and preferably are, employed as ingredients of yarn conditioning or lubricating formulas in conjunction with agents which function wholly or partially as lubricants.

In the following examples and description we have set forth several of the preferred embodiments of our invention, but they are included merely for purposes of illustration and not as a limitation thereof.

Example 1

The compound β-nitroethylricinoleate is applied to textile materials (silk, wool, viscose, cotton, cellulose acetate) by means of a wick, roller, spray, bath, pad, etc. to facilitate their knitting, weaving, spinning and the like. If the yarn is intended primarily for knitting, the amount of conditioning liquid applied may vary from 2–25% by weight of the yarn, and if for weaving between 1–5% by weight.

Example 2

A conditioning liquid is made up as follows:

	Parts
Di-β-nitropropylsuccinate	40
Olive oil	60

and applied to textile materials such as silk, wool, viscose, cellulose acetate, etc. as described in Example 1. If the yarn is intended primarily for knitting, the amount of conditioning liquid applied may vary from 2–25% by weight of the yarn, and if for weaving, between 1–5% by weight.

Other examples of yarn conditioning compositions which may be applied to various types of yarns, particularly those composed of or containing cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate, and similar cellulose organic acid esters in accordance with our invention and which render such yarns soft and pliable and especially well adapted for various textile operations, particularly knitting, are as follows:

Example 3

	Parts
Blown olive oil	75
β-methyl-β-nitropropyladipate	25

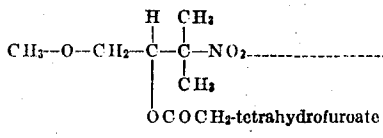
Example 4

	Parts
Light mineral oil	55
α-nitro-β-hydroxy-isodedecylacetate	40
Potassium oleate	5

Example 5

	Parts
Sperm oil	70
α-nitro-β-phenyl-β-hydroxyethyloleate	30

Example 6

	Parts
Blown sperm oil	40
Sperm oil	30
	30

OCOCH₂-tetrahydrofuroate

Example 7

	Parts
Neat's-foot oil	60
β-nitroethyl-β-hydroxyisobutyrate	40

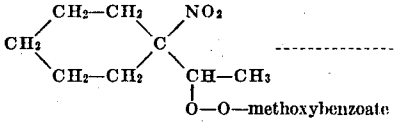
Example 8

	Parts
Blown sperm oil	80
β-tetrahydrofurfuryl-α-nitronaphthenate	20

Example 9

	Parts
α-nitroisopropyl succinate	20
Teaseed oil	30
Sulfonated castor oil	20
Mineral oil	10
Oleic acid	10
Ethanolamine	3
Water	7

Example 10

	Parts
	30

O—O—methoxybenzoate

Blown teaseed oil	50
Sulfonated castor oil	15
Sodium sulfate	2
Water	3

Example 11

	Parts
β-methoxyethylsuccinate	20
β-nitroethylphthalate	15
Blown neat's-foot oil	40
Oleic acid	15
Potassium oleate	5
Disodium phosphate	2
Water	3

Example 12

	Parts
2-methyl-2-nitroamyl acetate	20
Mineral oil	20
Tetrahydrofurfuryl acetal	20
Oleyl alcohol	20
Ethanolamine phosphate	5
Oleic acid	5

Example 13

A 20% solution of cellulose acetate in acetone in which is incorporated 1–25% by weight of β-nitroethylstearate is extruded through fine orifices into an evaporative atmosphere. The filaments thus produced are wound or twisted and wound. Yarns thus produced are of dull luster and suitable for knitting.

Example 14

	Parts
Water	80
β-nitro-β-ethylbutyllactate	10
Water-soluble cellulose ester or ether	5
Glycerol acetone	5

Any of the above compositions may be applied to the yarn intended for use in circular knitting by means of a bath, wick, spray, roller, pad or any suitable means. The amount of conditioning liquid applied may vary between 5–25% by weight of the yarn. Usually, however, the amount of conditioning liquid applied is about 10–15% by weight of the yarn. Yarn composed of cellulose acetate conditioned as described above gives excellent results when used in the circular knitting process.

As will be apparent from the above examples and description the conditioning agents of our invention may be applied by a wide variety of methods. For example, we may employ the agent as an ingredient of the spinning dope from which the filaments are formed, the amount of the agent so employed depending upon a number of factors, such as the particular cellulose derivative used in making the yarn, the solvent or solvent combination used in making up the spinning solution, and the degree of softness or pliability desired in the yarn, etc.

If the conditioning agent is to be applied to the yarn after spinning, this may be done by bringing the yarn in contact with a wick, roll, or felt wet therewith, or the liquid may be applied by immersion, spray, or otherwise. The particular point at which the liquid is applied may vary. It may, for example, be applied to the yarn inside or outside the spinning cabinet, between the guide and godet roll, between the godet or other roll or guide and the point of winding and/or twisting. In some cases, the liquid may even be applied to the yarn after winding onto cones, spools, bobbins, or the like or by the so-called "bobbin to bobbin" method. In the case of staple fiber manufacture, the liquid may be applied to the yarn prior to, or after cutting into staple lengths.

The amount of the agent so employed will vary widely depending upon the results desired, the specific nature of the material to which the agent is applied, the use to which the yarn is eventually to be put and other factors. For example, in a given case where a cellulose organic acid ester yarn such as a yarn composed of cellulose acetate, is intended for knitting, about 4 to 25% or more by weight, based on the weight of the dry yarn, may be satisfactory, while if the yarn is intended for weaving, the amount may vary between about 1 and 5%.

Although in the above examples we have referred primarily to yarn treating compositions containing only the conditioning agent and an oil, other ingredients such as solvents, non-solvents, emulsifying agents, blending agents and the like, may be added within the scope of our invention. Likewise, various dyes or other coloring matter may be included in case it is desired to permanently or fugitively tint or dye the material undergoing treatment.

Although we have found it convenient to illustrate our invention by reference to compositions containing specific percentages of the various ingredients, these percentages may vary widely depending upon the particular purpose for which the composition is intended. For example, if it is desired to control the solvent or softening action of the conditioning agent, the amount of the agent may be adjusted as, for example, by reducing the amount of the agent and correspondingly increasing the amount of oil or other ingredient.

While we have described our invention with

particular reference to the treatment of yarns composed of organic derivatives of cellulose such as cellulose acetate, the conditioning agents and formulas described herein are applicable to the conditioning of many other types of cellulose derivative yarns such as those composed of or containing cellulose propionate, cellulose butyrate, cellulose acetate propionate, cellulose acetate butyrate, ethyl cellulose, methyl cellulose, benzyl cellulose and others, as well as to the conditioning of silk, wool, cotton, viscose and other natural or artificial materials.

The term "yarn" as used herein and in the claims is to be understood as including a single filament, a plurality of filaments associated into the form of a thread, either of high or low twist, single or multiple threads associated or twisted together, composite threads composed of a mixture of natural and artificial filaments or a composite thread formed by twisting together individual strands of natural or artificial materials, as well as cut staple fibers produced from natural and/or artificial filaments or threads and spun yarn produced from such staple fibers.

As indicated above, the yarn conditioning agents of our invention are exceptionally good solvents for a wide variety of mineral, blown and unblown, drying and semi-drying animal and vegetable oils such as cottonseed, olive, castor, neat's-foot, sperm and other oils. This enables them to be used with any of such oils in making up a variety of yarn treating formulas of varying composition.

The yarn conditioning method and compositions of our invention possess many outstanding advantages. The fundamental and outstanding characteristic of the agents employed in accordance with the invention is their ability to soften yarns, especially those composed of or containing organic derivatives of cellulose such as cellulose acetate and render them soft and pliable and amenable to various textile operations, especially operations such as those involved in weaving and knitting where complicated designs or stitches are employed, without too drastic an action on the yarn material. Another outstanding characteristic of these compounds is their exceptional solvent power for a wide variety of mineral, animal, and vegetable oils and their ability to act as lubricating assistants in conjunction with these oils when applied to such yarns. In addition, due to their solubility in water, they may be readily removed from yarns and fabrics by means of the usual aqueous scour baths. By employing the yarn conditioning agents and method of our invention as herein described, one is enabled to obtain highly satisfactory results in the manufacture of yarns and woven fabrics and especially the production from these yarns of closely knit fabrics free from defects such as pin holes, stitch distortion, laddering and the like.

Use of Compounds as Plasticizers

The following examples illustrate preferred compounds in which the above-mentioned compounds are employed in accordance with our invention:

Example 15

	Parts
Cellulose acetate	100
β-Nitroethylsuccinate	80
Acetone	400

Example 16

	Parts
Cellulose acetate	100
β-Nitropropyl adipate	20
Methanol	100
Acetone	300

Example 17

	Parts
Cellulose acetate	100
β-Nitrobutyl maleate	30
Ethylene dichloride	300
Dioxane	100

Example 18

	Parts
Cellulose acetate	100
α-Nitro-iso-propyldiglycolate	30
Triphenyl phosphate	20
Acetone	300
Ethyl acetate	100

Example 19

	Parts
Cellulose acetate propionate	100
Butyl phthalate	20
β-Propyl-α-nitroethylsebacate	30
Propylene chloride	100
Ethyl lactate	100
Acetone	100

Example 20

	Parts
Cellulose nitrate	100
β-Nitroethyldiglycolate	30
Ester gum	40
Ethyl acetate	200
Toluene	100
Ethanol	100

Example 21

	Parts
Cellulose butyrate	100
β-Nitro-β-methylpropylmaleate	40
Propylene chloride	300
Acetone	100

Example 22

	Parts
Cellulose butyrate	100
β-Methyl-β-nitroamylphthalate	30
Triphenyl thiophosphate	10
Camphor	10
Ethylene chloride	400
Methanol	100

Example 23

	Parts
Ethyl cellulose	100
β-Nitroethyl citrate	40
Dioxane	400

Compositions of matter prepared as above described may be deposited upon any suitable film forming surface to form a film or sheet, as is well known to those skilled in the art. A film so produced has permanently brilliant transparency and low inflammability, burning no more readily than ordinary newsprint. Such film is exceedingly tough and flexible, as shown by the fact that it will withstand many folds upon a modified Schopper fold-tester (commonly used for such purposes) without breaking and that even after being subjected for a considerable number of days to air maintained at a temperature of 65° C. the film still maintains flexibility (in contrast to almost complete lack of flexibility where no plasticizer is used) demonstrating that the film will withstand ordinary usage satisfactorily for many

years. The sum total of the above advantageous properties of a product produced from our new composition is considerably in excess of that of products produced with what have previously been regarded as the better plasticizers.

Other similar solvents than those mentioned above which are compatible with cellulose acetate and our new plasticizers may also occur to those skilled in this art. In like manner our plasticizers may be compounded with other single or mixed organic esters of cellulose, such as cellulose aceto-stearate, aceto-malate, or cellulose nitro-acetate, the cellulose ethers and resins above mentioned, a suitable solvent which will dissolve both the cellulosic derivative and the plasticizer being employed.

Our novel plasticizers may be employed also with advantage in connection with a number of the known lacquer and varnish formulas with which it may be found to be compatible. In such cases the plasticizer is usually first put into solution with the cellulose derivative or resin solution and, if non-solvents are added, only to such an extent as will not precipitate the derivative or resin from solution. Also the plasticizer is usually employed in larger amounts, such as from 50 to 60 parts, in compounding lacquers. Other uses within the scope of our invention will also suggest themselves to those skilled in the art and are to be included within the scope of the claims appended hereto.

What we claim is:

1. The process of conditioning yarn to render it more amenable to textile operations including knitting, weaving, spinning and the like which comprises applying thereto a lubricating and softening composition containing as its essential lubricating and softening component an ester selected from the group consisting of the nitroalkane and nitroalkene esters of mono- and poly-carboxylic, aliphatic, aromatic and heterocyclic acids.

2. The process of conditioning yarn composed of or containing organic derivatives of cellulose to render it more amenable to textile operations including knitting, weaving, spinning and the like, which comprises applying thereto a lubricating and softening composition containing as its essential lubricating and softening component an ester selected from the group consisting of the nitroalkane and nitroalkene esters of mono- and poly-carboxylic, aliphatic, aromatic and heterocyclic acids.

3. The process of conditioning yarn composed of or containing cellulose acetate to render it more amenable to textile operations including knitting, weaving, spinning and the like, which comprises applying thereto a lubricating and softening composition containing as its essential lubricating and softening component an ester selected from the group consisting of the nitroalkane and nitroalkene esters of mono- and poly-carboxylic, aliphatic, aromatic and heterocyclic acids.

4. The process of conditioning yarn composed of or containing cellulose acetate to render it more amenable to textile operations including knitting, weaving, spinning and the like, which comprises applying thereto a lubricating and softening composition containing as its essential lubricating and softening component an ester selected from the group consisting of the nitroalkane and nitroalkene esters of mono- and poly-carboxylic, aliphatic, aromatic and heterocyclic acids, and a textile lubricant.

5. A conditioning agent for rendering yarns more amenable to textile operations including knitting, weaving, spinning and the like which comprises an ester selected from the group consisting of the nitroalkane and nitroalkene esters of mono- and poly-carboxylic, aliphatic, aromatic and heterocyclic acids.

6. A conditioning agent for rendering textile yarns composed of or containing organic derivatives of cellulose more amenable to textile operations including knitting, weaving, spinning and the like which comprises an ester selected from the group consisting of the nitroalkane and nitroalkene esters of mono- and poly-carboxylic, aliphatic, aromatic and heterocyclic acids, and a textile lubricant.

7. Textile yarns amenable to textile operations including knitting, weaving, spinning and the like impregnated with a lubricant containing as its essential lubricating and softening component an ester selected from the group consisting of the nitroalkane and nitroalkene esters of mono- and poly-carboxylic, aliphatic, aromatic and heterocyclic acids.

8. Textile yarns composed of or containing organic derivatives of cellulose amenable to textile operations including knitting, weaving, spinning and the like, impregnated with a conditioning agent comprising an ester selected from the group consisting of the nitroalkane and nitroalkene esters of mono- and poly-carboxylic, aliphatic, aromatic and heterocyclic acids.

9. Textile yarns composed of or containing organic derivatives of cellulose amenable to textile operations including knitting, weaving, spinning and the like, impregnated with a conditioning agent comprising an ester selected from the group consisting of the nitroalkane and nitroalkene esters of mono- and poly-carboxylic, aliphatic, aromatic and heterocyclic acids, and a textile lubricant.

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