

UNITED STATES PATENT OFFICE

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THIOGLYCOL ESTERS

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The present invention is directed to thioglycol esters and more particularly to compounds of this character which find utility in various commercial applications.

In the prior art, various esters of thiodiglycol and other thiopolyglycols have been known. For instance, esters of such glycols with lower fatty acids having from 1 to 4 carbon atoms have been proposed as plasticizers for synthetic rubber. Also, esters of certain fatty acids having from 7 to 9 carbon atoms in the molecule with thiodiglycol have been proposed as softening agents for incorporation into certain vinyl ester resins and the like. None of the esters heretofore proposed have had any extended application, most likely because the properties of such esters did not render them suitable or superior for the intended purposes.

The present invention is intended and adapted to provide esters of thioglycols which have excellent properties for incorporation in various synthetic resinous or similar materials such as the vinyl resins and synthetic rubbers.

It is also among the objects of the present invention to provide partial esters of thioglycols which shall have desirable properties for use as emulsifiers, dispersing agents, wetting agents and the like.

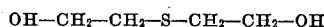
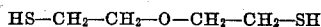
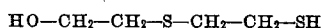
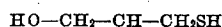
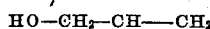
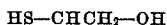
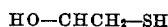
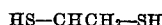
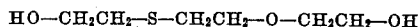
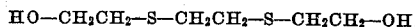
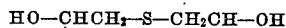
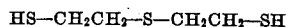
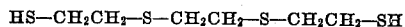
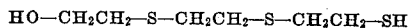
In practicing the present invention, I may provide a thiomonoglycol wherein the alkyl radical has a small number of carbon atoms preferably within the range of 2 to 6 carbon atoms. The thiomonoglycol also includes thiomonoglycerol and like substances. Compounds of this type are reacted with fatty acids having from 6 to 18 carbon atoms. The reaction products may be of single acids with the glycol or mixtures of such acids may be reacted therewith. Several such mixtures have been found especially suitable such as a fraction of coconut oil fatty acids wherein lauric acid is the principal constituent and a different fraction of coconut oil fatty acids wherein caprylic acid is the major constituent. In general, the acids which may be used for reaction with the thiomonoglycol include n-caproic acid, 2-ethylbutyric acid, enanthic, caprylic, 2-ethylhexoic, pelargonic, capric, lauric, myristic, palmitic, stearic, oleic, linoleic, linolenic, etc. Mixtures of these acids may be used, and in particular, mixtures of acids such as are obtained from natural fats and oils or from various fractions thereof, may be used. Compounds of this character are excellent plasticizers for synthetic resins, cellulose products, rubbers, etc., while partially esterified compounds of this character are

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quite useful in industry and might be utilized as wetting agents, dispersing agents, emulsifiers and detergents.

The present invention also contemplates certain esters of the thiopolyglycols. It has been found that the higher fatty acids having from 12 to 18 carbon atoms and higher, namely, those acids which are found in natural glyceride oils and synthetic acids having the same numbers of carbon atoms, may be reacted to give substantially neutral esters wherein two molecules of the acid and one molecule of the thiopolyglycol react. Also, mixtures of such acids may be used and particularly a mixture containing lauric acid as the major constituent has been found to give products having especially valuable properties. In general, esters of this type are excellent softening agents or plasticizers for synthetic resins, rubbers and the like. A relatively small amount of such softening agent is capable of imparting desirable characteristics to the substances being plasticized.

The following are typical substances which may be utilized in the present invention:



While a considerable number of the polyglycols are listed above as typical substances to be used in making the esters of the present invention, they

illustrate the large numbers thereof which are available. Still other substances of the general character may be used in place thereof in the described reactions. The polyglycols may contain other elements and configurations than those specifically named herein which will allow the described reactions to proceed.

The esters may be prepared in a variety of ways, including direct esterification of the thio-glycols with the desired fatty acid or mixture of acids, by reaction of the thioglycols with fatty acid chlorides or anhydrides, by ester interchange between other fatty acid esters and thioglycols, or in the case of thiodiglycol also by direct reaction between β, β' -dichlorodiethyl sulfide (mustard gas) and the salts of the fatty acids.

The following examples illustrate methods of preparation and application of these plasticizers.

Example I

A mixture is made of 1 mol. of thiodiglycol with 2 mols. of a mixture of fatty acids obtained by fractionating the free fatty acids of coconut oil having the following composition:

	Per cent
Lauric acid.....	63
Myristic acid.....	25
Palmitic acid.....	12

The mixture is heated at temperatures up to 225° C. whereby a reaction takes place with the elimination of water. The water is removed continuously from the reaction mass by evaporation and the heating is continued at about the maximum temperature until the free fatty acid value calculated as oleic acid has fallen to about 4. The substantially neutral ester thus formed is then refined by methods known in the art including a washing with an aqueous alkali solution, the product being a low melting solid. If necessary or desirable, the product may be bleached and otherwise further refined. The product has the formula $ROCH_2CH_2SCH_2CH_2OR$, wherein R is a lauric, myristic or palmitic acid radical.

Example II

One mol. of thiomonoglycol, which is prepared from ethylene chlorohydrin and sodium hydrosulfide, is mixed with 1 mol. of a fraction obtained from the distillation of the free fatty acids of coconut oil having the following composition:

	Per cent
Capric acid.....	40
Caprylic acid.....	54
Caproic acid.....	6

The esterification reaction is conducted in approximately the manner set forth in Example I, the product being a neutral light-colored oil. The product has the formula $RSCH_2CH_2OH$, wherein R is a capric, caprylic or caproic acid radical.

Example III

A mixture is made of 2 mols. of the methyl ester of lauric acid and 1 mol. of thiotriglycol. To this is added a solution of 0.1% of sodium methoxide in methyl alcohol. The mixture is heated to a temperature of about 200° C. under a short fractionation column. As the reaction proceeds, methyl alcohol is formed and is continuously removed in the vapor state through the column. The heating is continued until no more methyl alcohol is released, indicating the end of the esterifying reaction. The residue is neutralized with aqueous hydrochloric acid, washed twice

with water and dried. The final product is a clear slightly yellow solid having a free fatty acid value below 0.3 calculated as oleic acid. This product gives strong highly elastic compositions when blended with a vinyl chloride and vinylidene chloride copolymer in a proportion of about 30%. Such composition retains its flexibility down to very low temperatures. The product has the formula $ROCH_2CH_2SCH_2CH_2OCH_2CH_2OR$, wherein R is a lauric acid radical.

Example IV

The product of Example III is blended in a proportion of 30 parts per 100 with polyvinyl butyral on a hot roll, giving a strong, homogeneous sheet, from which thin sections were cut and incorporated between glass sheets to give a safety glass composition. This composition is much stronger and impact-resistant than glass sheets of equal thickness, and on breaking, the broken pieces of glass adhered strongly to the interlayer. This feature is extremely desirable for the automotive and airplane industries. Moreover, these properties are retained over a wide range of temperature, as, for example, from 180° F. to -20° C., thus giving stable compositions which would be useful in hot climates as well as in cold areas.

Example V

Ten parts of the diester of thiomonoethylene glycol with capric acid is incorporated as the sole plasticizer in a tire tread stock based on GR-S synthetic rubber (copolymerized butadiene and styrene). Incorporation on the mill is easy and rapid and gives a smooth product of good handling properties. On vulcanization for 40 minutes at 300° F., a dry vulcanizate which is strong and has good elongation and abrasion resistance is obtained. This product remains soft and flexible to low temperatures.

Example VI

A monoester of thiodiglycol and lauric acid is prepared by mixing one mol. of each of these materials and heating in a current of carbon dioxide until the theoretical amount of water has been liberated. The resulting low-melting solid is an excellent emulsifying agent.

Example VII

A monoester of monothioglycerol and stearic acid is produced by essentially the same procedure as in Example VI. The solid product is very useful as a blending and emulsifying agent in the formulation of cosmetic creams, waxes, powders, pastes, etc.

Esters of the thiomonoglycol with natural and synthetic caproic and caprylic acids give excellent plasticizing action in polyvinyl butyral compositions such as are used as interlayers for safety glass.

Similar esters, but of the higher molecular weight acids, such as the dilaurate, or mixed caprate-laurate, with thioglycols have proved to be excellent plasticizers for the synthetic rubbers, including butadiene copolymers with styrene, acrylonitrile, etc., polyalkylene polysulfides, polyisobutylene, polychloro-butadiene, etc. In general, these plasticizers have a surprisingly high degree of compatibility with the aforementioned resins, and small percentages produce large softening actions.

Further, it has been found that these softening actions are maintained down to very low temperatures (40 to 50 degrees below zero, Fahrenheit).

heit), so that the plasticized compositions have a wide range of utility. In addition, their high boiling points give them excellent stability in compositions which may be exposed to high temperatures and where low volatility is of prime importance, as in fabric coatings where the fabrics are exposed to tropical heat and direct sunshine, etc.

Monoesters of these and other acids with the mentioned alcohols are also excellent plasticizers, but generally are somewhat more volatile than the diesters, and preferably should be used where this greater volatility will not be a serious drawback.

In addition, many of these monoesters have demonstrated excellent emulsifying and blending properties which make them useful in many applications, including wetting agents, dispersing agents for oils in aqueous systems, detergents, cosmetics, polishes, protective waxes, insecticides, textile finishes, lubricants, etc.

Although the invention has been described by the use of a number of specific examples, the invention is not limited thereby but such examples are to be considered as illustrative of the breadth of the invention. While several specific mixtures of acids which are reacted with the thioglycols have been named, various other mixtures may also be provided and the acids may be synthetic as well as natural. Mixtures may be made of acids having even and odd numbers of carbon atoms and in general it is preferable that such mixtures be made from fatty acids with adjacent or nearly adjacent numbers of carbon atoms. The methods used in the production of the esters may be varied as the details of the manipulation are well-known to the chemist. Also, the products of the present invention are compatible for uses other than those set forth herein.

These and other changes in the details of the invention may be made within the spirit thereof, the scope of which is to be broadly construed and not to be limited except by the character of the claims appended hereto.

I claim:

1. An ester of a thioglycol having at least one sulphhydryl group with a higher fatty acid having from 12 to 18 carbon atoms.
2. An ester of a thioglycol ether having at least one sulphhydryl group with a higher fatty acid having from 12 to 18 carbon atoms.
3. An ester of a thioglycol thio-ether having at least one sulphhydryl group with a higher fatty acid having from 12 to 18 carbon atoms.
4. An ester of a thioglycol having at least one sulphhydryl group with a mixture of at least two higher fatty acids having from 12 to 18 carbon atoms.
5. An ester of a thioglycol having at least one sulphhydryl group with a mixture of at least two higher fatty acids having from 12 to 18 carbon atoms, said mixture containing a major proportion of lauric acid and the remainder being myristic and palmitic acids.
6. An ester of a thioglycol having at least one sulphhydryl and one hydroxyl group with a higher fatty acid having from 12 to 18 carbon atoms.

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