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## COMPOSITION AND PROCESS FOR RENDERING TEXTILE FABRICS WATER-REPELLENT

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This invention relates to an improved process and composition for imparting water-repellent properties to textile materials.

As disclosed in U. S. Patent 2,211,976 to Hubert et al, reaction of monocarboxy acid amides with formaldehyde yields methylolamides of the carboxy acids having the formula

$$R—CO—N(R')—CH_2OH$$

wherein R—CO— is the acyl radical of the carboxylic acid and R' is hydrogen or an aliphatic hydrocarbon radical. These compounds, particularly those in which the radical R—CO— is an aliphatic or alicyclic radical containing 5 or more carbon atoms, impart hydrophobic properties to textile materials, especiallly cellulosic material when applied thereto in organic solvent solution or aqueous emulsion, and "cured" under mild acidic conditions on the fiber by heating at elevated temperatures, e. g. of the order of 110 to 140° C. The methylolamides of higher fatty acids corresponding to the natural fatty glycerides are especially adapted for this purpose. As disclosed in U. S. Patent 2,431,202 to Sanders, such methylolamides can be combined advantageously with aqueous emulsifying agents to form dry compositions yielding, upon addition to water, emulsions suitable for impregnating textile materials.

U. S. Patent 2,189,648 to Guenther discloses preparation of derivatives of higher aliphatic carboxy methylolamides, formed by reaction of such methylolamides with sulfur dioxide and a tertiary nitrogen base such as pyridine or a trialkylamine, whereby a carboxyamido-methyl quaternary ammonium sufite is apparently formed which is soluble in water, and which possesses dispersing and emulsifying properties. These compounds, when impregnated on textile materials, and heated, apparently decompose, yielding a water-repellent finish similar to that of the corresponding carboxy acid methylolamides. It was also known that other higher molecular weight quaternary ammonium compounds would yield water-repellent finishes on textiles, especially quaternary ammonium compounds containing a fatty acid amido-methylene radical attached to the quaternary or pentavalent nitrogen atom.

Water-repellent finishes produced by impregnation of textile materials by the foregoing procedures, while often highly effective initially, suffer substantial loss in effectiveness upon subjecting the material to washing or dry cleaning.

In general, the emulsifying agents heretofore

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suggested for the methylolamides of carboxy acids acted merely as media for application and were normally removed in washing or other processing of the impregnated material. While some quaternary ammonium salts have been employed as dispersing agents for methylolamides of higher fatty acids for impregnation of textile materials, serious discolorations often result in the curing of the composition on the textile materials.

It is an object of this invention to provide a novel method and composition for producing a water-repellent finish on textile materials of outstanding resistance to washing and dry cleaning, such compositions being emulsifiable in water to yield emulsions suitable for impregnation, and causing no objectionable discoloration of the textile materials on curing by heating at elevated temperatures. We have discovered that methylolamides of higher aliphatic carboxylic acids such as those corresponding to the natural fatty glycerides, when combined with certain water-soluble quaternary ammonium compounds, hereinafter more fully described, yield compositions which readily form emulsions in water, suitable for impregnation of textile materials. When thus applied and cured by heating in the known manner, a water-repellent finish is produced of which the resistance to washing and dry cleaning is unexpectedly enhanced as compared with the effectiveness of either of the ingredients of the composition, and at the same time, the finish produced has no serious disadvantages such as discoloration or yellowing of light-colored fabrics.

In accordance with this invention, methylolamides of carboxy acids of the type heretofore disclosed in U. S. Patents 2,211,976 and 2,,306,185, but preferably methylolamides of higher fatty acids corresponding to those of the natural fatty glycerides, particularly straight-chain aliphatic carboxy acids containing 8 to 18 carbon atoms, are combined with a water-soluble quaternary ammonium salt, especially a halide or a sulfite including a tertiary nitrogen base such as pyridine, or a tertiary amine such as trimethylamine, triethylamine, dimethylaniline and the like, containing as one substituent of the nitrogen a higher aliphatic or aliphatic-aromatic group joined to the nitrogen by a methylene radical, such compounds having the general formula

$$A—CH_2—N(tert)—X$$

wherein A is a radical of the class consisting of alkyl carboamido radicals of 8 to 18 carbon

atoms, higher alkoxy radicals of 8 to 18 carbon atoms, higher alkoxy mono- and polyethenoxy ether radicals in which the alkoxy group contains 8 to 18 carbon atoms, and containing 1 to 3 ethenoxy groups, higher fatty acid esters of hydroxy mono- and polyethenoxy ether radicals in which the fatty acid radical contains 8 to 18 carbon atoms and containing 1 to 3 ethenoxy groups, and nuclear alkyl-substituted phenoxy mono- and polyethenoxy ether radicals in which the nuclear alkyl groups contain a total of 5 to 18 carbon atoms, N(tert) represents the radical of tertiary nitrogen base, and X represents a salt-forming anion of a volatile acid.

The radicals represented by A in the last three classes of compounds mentioned above which contain ethenoxy groups may be represented by the general formula

$$A'—O(CH_2—CH_2—O—)_n$$

wherein A'—O— represents a higher alkoxy, higher fatty acyloxy or alkyl-substituted phenoxy radical as defined above, and $n$ represents an integer from 1 to 3.

In order to prepare the compositions of the invention, the aforesaid methylolamides, preferably in molten form, are mixed with the aforesaid quaternary nitrogen compounds to form a homogeneous mass, preferably by mixing with a water-miscible volatile mutual solvent or blending agent, such as a lower aliphatic monohydric alcohol (e. g. methanol, ethanol, propanol or isopropanol), one or more of the ingredients being heated, if necessary, to facilitate formation of a homogeneous mass. On cooling, a self-emulsifying paste is obtained which can be conveniently added in measured amounts to water to form an aqueous impregnating bath for textiles.

The proportion of the quaternary ammonium compounds employed in accordance with the invention to the fatty acid methylolamides is such as to yield a stable emulsion of the latter when the mixture is added to water. For this purpose, the weight ratio of the aforesaid components is from 2:1 to 1:4 and preferably from 1:1 to 1:2. In preparing the compositions with a blending agent, the water-soluble alcohols mentioned above can be conveniently used in amounts approximately equal to the combined weight of the quaternary ammonium compound and fatty acid methylolamide which constitute the other ingredients of the composition.

In applying the compositions of the invention for rendering textile materials water-repellent, the compositions prepared as described above are added to water or an aqueous impregnating bath such that the concentration of the active ingredients (the higher fatty acid methylolamide, and the quaternary ammonium compound serving as the emulsifying agent), is from about 1 to 10%, and preferably 3 to 8%, of the bath. The textile material is impregnated with the resulting bath, dried, and cured at a temperature from 120 to 250° C. for a period ranging from 10 minutes to 45 seconds. Shorter periods are employed, the higher the temperature. A water-repellent finish is thus obtained without discoloration or other injury of the material, which has unexpectedly increased resistance to washing and dry cleaning as compared with a similar finish produced with the respective ingredients of the composition employed alone in comparable concentrations.

Preparation of a number of compositions in accordance with this invention, and application thereof to textile materials is illustrated in the following examples wherein parts and percentages are by weight.

*Example 1*

Methylolstearamide is prepared by heating a mixture of 1320 parts of stearamide with 154 parts of paraformaldehyde at 125 to 130° C. for 30 minutes. 660 parts of a quaternary nitrogen compound base salt, prepared by passing sulfur dioxide into a mixture of methylolstearamide and pyridine, as disclosed in U. S. Patent 2,189,643, is dissolved in 1980 parts of isopropyl alcohol, and the methylolstearamide, obtained as indicated above, is melted and added to the isopropyl alcohol solution with good agitation. A light tan colored paste is obtained which readily forms an emulsion on addition to water. One part of this paste is added to 10 parts of water, and cotton cloth passed through the water emulsion and squeezed through rubber rollers to remove the excess. The cloth is dried at 80° C. and cured by heating for 3 minutes at 150° C. The water-repellency thus produced withstands repeated washings and dry cleanings.

*Example 2*

33 parts of methylolstearamide, prepared as disclosed in Example 1, are melted and added to a solution of 17 parts of diamylphenoxyethoxy-methyl pyridinium chloride in 50 parts of isopropyl alcohol. The paste thus formed is added to 1000 parts of water, and the resulting emulsion applied to cotton cloth in the same manner as in Example 1. On drying and curing, an excellent water-repellent finish is obtained of outstanding permanence to washing and dry cleaning.

*Example 3*

33 parts of molten methylolstearamide are added to a solution of 17 parts of dodecylphenoxyethoxy-methyl pyridinium chloride in 50 parts of isopropyl alcohol. The paste thus formed is dispersed in water as in the preceding examples and similarly applied for the production of a water-repellent finish on cotton cloth. The finish produced is likewise of outstanding fastness to washing and dry cleaning.

Similar results are obtained by substituting octadecylphenoxyethoxy - methyl pyridinium chloride or triethyl ammonium chloride, in similar amounts, for the dodecylphenoxyethoxyethyl pyridinium chloride of the composition described in this example.

*Example 4*

33 parts of molten methylolstearamide are added to a solution in 50 parts of isopropyl alcohol of 17 parts of β-stearoyloxyethoxy-methyl pyridinium chloride (prepared by reaction of ethylene glycol monostearate with paraformaldehyde and hydrochloric acid to form β-stearoyloxyethoxy-methyl chloride, and reaction of the latter with pyridine to form the corresponding pyridinium chloride). The resulting paste disperses readily in water in the proportions used in the foregoing examples, and when applied to textile material and cured in similar manner to that described above, yields an excellent water-repellent finish of outstanding resistance to washing and dry cleaning.

*Example 5*

50 parts of molten methylolstearamide are added to a solution in 100 parts of isopropyl alcohol of 50 parts of stearoyl-amidomethyl-triethyl

ammonium-triethylamine sulfite obtained according to U. S. Patent 2,189,648 from stearamide, paraformaldehyde, triethylamine and sulfur dioxide. The paste formed in this manner disperses readily in warm water to form an impregnating bath which is applied to textile materials as in the preceding examples. When cured at elevated temperatures in the manner described above, an excellent water-repellent finish is produced, similar in properties to the finish produced in the preceding examples.

Each of the compositions prepared in accordance with Examples 1, 2, 3 (the first product) and 4 were added to water in sufficient amount to yield a 5% solution of the active ingredients (i. e., the methylolstearamide and the quaternary dispersing agent), and the resulting dispersions were applied to cotton cloth by the method of Example 1. For purposes of comparison, 5% aqueous solutions of the quaternary dispersing agents contained in said compositions, but without methylolstearamide, were prepared and similarly applied to cotton cloth. A solution of methylolstearamide in isopropyl alcohol, containing 5 parts by weight of methylolstearamide per 100 parts by volume of the alcohol (1 part by volume being equal to the volume of 1 part by weight of water) was impregnated on cotton cloth and dried. Each of the impregnated samples of cloth were cured under the conditions set out in the foregoing examples. The samples were then subjected to comparative tests for water repellency (by the standard spray rating method described in "Technical Manual and Yearbook of the American Association of Textile Chemists and Colorists," vol. 24, 1947–8, page 147), directly after curing, and likewise after an alkaline rinse, as well as after three successive laundering treatments, and after three successive dry cleaning treatments with a petroleum hydrocarbon dry cleaning solvent. The water-repellency of the samples was rated on a scale in which 100 corresponds to complete water-repellency, and zero to no repellency. The results thus obtained on the aforesaid scale were as follows:

| | After Curing | After Alkaline Rinse | After Successive Laundering | | | After Successive Dry Cleaning | | |
|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 1 | 2 | 3 |
| Composition of: | | | | | | | | |
| Example 1 | 100 | 100 | 80 | 80 | 70 | 100 | 90 | 90 |
| Example 2 | 100 | 100 | 80 | 70 | 70 | 70 | 70 | 70 |
| Example 3 | 100 | 100 | 90 | 70 | 70 | 80 | 80 | 70 |
| Example 4 | 100 | 100 | 80 | 70 | 70 | 100 | 90 | 90 |
| Methylol-stearamide | 100 | 100 | 50 | 50 | 50 | 50 | 50 | 50 |
| Quaternary Compound of: | | | | | | | | |
| Example 1 | 100 | 90 | 80 | 70 | 50 | 70 | 70 | 50 |
| Example 2 | 50 | 50 | 50 | 0 | 0 | 50 | 0 | 0 |
| Example 3 | 70 | 70 | 50 | 50 | 50 | 50 | 50 | 50 |
| Example 4 | 50 | 50 | 50 | 0 | 0 | 50 | 50 | 0 |

As indicated by the results of the foregoing tests, the water-repellent finishes produced by the respective active ingredients of the compositions of the invention are decidedly inferior, in resistance to washing and dry cleaning, to the finishes produced by the combination of said ingredients in the compositions of the invention. While methylolstearamide and the quaternary compound of Example 1 provide similarly high initial water-repellency as compared with the compositions of the invention, and methylolstearamide alone provides comparable resistance after an alkaline rinse, the quaternary compounds used alone provide inferior water-repellency in every case, and likewise after the alkaline rinse.

The compounds of the compositions illustrated in the examples are not limited to those specified therein. Thus, instead of N-methylolstearamide, there can be used the N-methylolamides of other carboxy acids, especially of the fatty acids of naturally occurring fatty glycerides, such as the N-methylolamides of lauric, margaric, oleic, ricinoleic, palmitic, and similar acids.

Instead of the quaternary nitrogen base salts of the foregoing examples, there can be used similar quaternary salts such as the alkylphenoxy mono- and polyethenoxy-methyl quaternary ammonium salts described in my copending application Serial No. 65,725 of December 16, 1948, and now abandoned, e. g. 2,4,6-triisopropylphenoxyethoxymethyl pyridinium chloride and para-(2,4,4-trimethylamyl-2)-phenoxy-ethoxymethyl-benzyl-dimethyl ammonium chloride.

Instead of the foregoing alkylated phenol ethers of hydroxy mono- or polyethenoxy-methyl quaternary ammonium bases, corresponding ethers in which the alkylphenoxy radical is replaced by a higher alkyl group of 8 to 18 carbon atoms, e. g. decyl, dodecyl, tetradecyl, oleyl, stearyl, or lauryl radicals, can be used. Similarly, higher alkyl ethers of hydroxy-methyl tertiary nitrogen base salts can be used such as lauryl, stearyl, decyl, dodecyl, tetradecyl and hexadecyl ethers of hydroxy-methyl pyridinium chloride.

Other higher fatty acid esters of hydroxy mono- and polyethenoxy-methyl quaternary ammonium compounds of the type disclosed in Example 4 can also be used, as, for example, decanoyl, lauroyl, margaroyl, oleyl, or palmitoyl-oxyethoxy or polyethoxymethyl pyridinium chloride, or trimethyl ammonium chloride, or triethyl ammonium triethylamine sulfite or dimethylbenzyl ammonium bromide.

Quaternary compounds derived from a higher fatty acid amide, formaldehyde, a tertiary nitrogen base and an acid, such as the products of U. S. Patent 2,189,648, obtained from sulfur dioxide, pyridine or triethylamine, paraformaldehyde and higher fatty acid amides, or by similarly reacting hydrogen chloride instead of sulfur dioxide with the other reagents, can be used as the dispersing agents of the present composition.

The tertiary nitrogen bases employed in the preparation, or included in the structure of the dispersing agents of the instant compositions, having the general formula given above in which they are represented by N(tert), can be heterocyclic bases such as pyridine, piccolines, lutidines, N-alkylpyrrol, its α-methyl derivatives, N-methyl morpholine, N-methyl piperidine, N-benzyl piperidine, quinoline, and tertiary alkyl, aryl, aralkyl or cycloalkyl-amines, such as trimethyl-, triethyl-, tributyl-, triamylamines N,N-dimethylethanolamine, N-methyldiethanolamine, triethanolamine, dimethylaniline, dimethylcyclohexylamine, or benzyldiethylamine.

The salt-forming anion of the quaternary ammonium salt employed as the dispersing agent is preferably that of a volatile inorganic acid such as sulfurous, hydrochloric or hydrobromic acid. In the case of polybasic sulfurous acid, the second hydrogen is advantageously neutralized by a second molecule of the tertiary amine, represented by N(tert) in the formula given above and included in the structure of the quaternary ammonium compound.

As hereinbefore stated, the proportions of the quaternary dispersing agent to the higher fatty acid methylolamide can be varied from about

2:1 to 1:4 to provide outstanding water-repellent properties and at the same time, satisfactory aqueous dispersion of the fatty acid methylolamide employed. The proportion of blending agent, which is especially a water-miscible monohydric alcohol, can be about the same as the amount of the other ingredients included in the composition. While any method suitable for homogeneous mixing of the ingredients can be used, the method described in the examples, wherein the methylolamide of a higher fatty acid is melted and added with agitation to a solution of the quaternary nitrogen base salt in the solvent employed as a blending agent, is a particularly convenient procedure.

In impregnating textiles, the proportion of composition added to the aqueous impregnating bath can be sufficient to yield a concentration of 1 to 10% of the active ingredients, and preferably from 3 to 8% in the bath. The impregnation of textiles can be carried out by any convenient method, e. g. by padding the material with the impregnating bath and squeezing out the excess carried by the fiber. The impregnated material is dried and cured by heating at temperatures from 120 to 250° C. for 10 minutes to 45 seconds, the period of heating being shorter for higher temperatures within the aforesaid range.

While the examples are directed to impregnation of cotton, other cellulosic fibers such as regenerated cellulose materials, and also textiles of other materials such as wool or other animal fibers, or synthetic fibers such as nylon can be impregnated in the same manner and the finish cured to render the textile material water-repellent and stable to washing and dry cleaning.

Variations and modifications which will be obvious to those skilled in the art can be made in the processes and compositions hereinbefore disclosed without departing from the scope or spirit of the invention.

We claim:

1. A composition for rendering textile materials water-repellent, which essentially consists of a higher fatty acid N-methylolamide homogeneously mixed with a quaternary nitrogen base salt having the general formula

$$A—CH_2—N(tert)—X$$

wherein A is a radical of the class consisting of alkyl carboamido radicals of 8 to 18 carbon atoms, higher alkoxy radicals of 8 to 18 carbon atoms, higher alkoxy mono- and polyethenoxy ether radicals in which the alkoxy group contains 8 to 18 carbon atoms and containing 1 to 3 ethenoxy groups, higher fatty acid esters of hydroxy mono- and polyethenoxy ether radicals in which the fatty acid radical contains 8 to 18 carbon atoms and containing 1 to 3 ethenoxy groups, and nuclear alkyl-substituted phenoxy mono- and polyethenoxy ether radicals in which the nuclear alkyl groups contain a total of 5 to 18 carbon atoms, N(tert) represents the radical of a tertiary nitrogen base, and X represents a salt-forming anion of a volatile acid, the ratio of the amount of said fatty acid N-methylolamide to said quaternary nitrogen base salt being from 1:2 to 4:1.

2. A composition as defined in claim 1, wherein the ratio of the amount of said fatty acid N-methylolamide to said quaternary nitrogen base salt is from 1:1 to 2:1, said composition further containing a water-miscible volatile organic blending agent for said components.

3. A composition as defined in claim 2, wherein said water-miscible blending agent is an aliphatic monohydric alcohol, the amount of said alcohol being approximately equal to the amount of the other aforesaid ingredients of said composition.

4. A composition for rendering textile materials water-repellent, which essentially consists of methylolstearamide and stearoylaminomethyl pyridinium pyridine sulfite, the ratio of the amounts of said components being from 1:1 to 2:1, and isopropyl alcohol in an amount approximately equal to the amounts of the aforesaid ingredients.

5. A composition for rendering textile materials water-repellent, which essentially consists of methylolstearamide and diamylphenoxyethoxymethyl pyridinium chloride, the ratio of the amounts of said components being from 1:1 to 2:1, and isopropyl alcohol in an amount approximately equal to the amounts of the aforesaid ingredients.

6. A composition for rendering textile materials water-repellent, which essentially consists of methylolstearamide and dodecylphenoxyethoxymethyl pyridinium chloride, the ratio of the amounts of said components being from 1:1 to 2:1, and isopropyl alcohol in an amount approximately equal to the amounts of the aforesaid ingredients.

7. A composition for rendering textile materials water-repellent, which essentially consists of methylolstearamide and β-stearoyloxyethoxymethyl pyridinium chloride, the ratio of the amounts of said components being from 1:1 to 2:1, and isopropyl alcohol in an amount approximately equal to the amounts of the aforesaid ingredients.

8. A composition for rendering textile materials water-repellent, which essentially consists of methylolstearamide and stearoylamidomethyl triethyl ammonium triethylamine sulfite, the ratio of the amounts of said components being from 1:1 to 2:1, and isopropyl alcohol in an amount approximately equal to the amounts of the aforesaid ingredients.

9. A process for rendering textile materials water-repellent, which comprises impregnating the textile material with an aqueous dispersion containing 1 to 10% of a composition consisting essentially of a higher fatty acid N-methylolamide, and as the dispersing agent therefor, a quaternary nitrogen base salt having the general formula

$$A—CH_2—N(tert)—X$$

wherein A is a radical of the class consisting of the alkyl carboamido radicals of 8 to 18 carbon atoms, higher alkoxy radicals of 8 to 18 carbon atoms, higher alkoxy mono- and polyethenoxy ether radicals in which the alkoxy group contains 8 to 18 carbon atoms and containing 1 to 3 ethenoxy groups, higher fatty acid esters of hydroxy mono- and polyethenoxy ether radicals in which the fatty acid radical contains 8 to 18 carbons atoms and containing 1 to 3 ethenoxy groups, and nuclear alkyl-substituted phenoxy mono- and polyethenoxy ether radicals in which the nuclear alkyl groups contain a total of 5 to 18 carbon atoms, N(tert) represents the radical of a tertiary nitrogen base, and X represents a salt-forming anion of a volatile acid, the ratio of the amount of said fatty acid N-methylolamide to said quaternary nitrogen base salt being from 1:2 to 4:1; drying the impregnated material, and heating to a temperature from 120 to 250° C. for a period ranging from 10 minutes to 45 seconds.

10. A process as defined in claim 9, wherein said aqueous dispersion contains 3 to 8% by

weight of said composition, and the weight ratio of the aforesaid components thereof is from 1:1 to 2:1.

11. A process for rendering textile materials water-repellent, which comprises impregnating the textile material with an aqueous dispersion containing 3 to 8% of a composition consisting essentially of methylolstearamide and, as the dispersing agent therefor, stearoylaminomethyl pyridinium pyridine sulfite, the ratio of said methylolstearamide to said sulfite being from 1:1 to 2:1, drying the impregnated material, and heating to a temperature from 120 to 250° C. for a period ranging from 10 minutes to 45 seconds.

12. A process for rendering textile materials water-repellent, which comprises impregnating the textile material with an aqueous dispersion containing 3 to 8% of a composition consisting essentially of methylolstearamide and, as the dispersing agent therefor, diamylphenoxyethoxymethyl pyridinium chloride, the ratio of said methylolstearamide to said pyridinium chloride being from 1:1 to 2:1, drying the impregnated material, and heating to a temperature from 120 to 250° C. for a period ranging from 10 minutes to 45 seconds.

13. A process for rendering textile materials water-repellent, which comprises impregnating the textile material with an aqueous dispersion containing 3 to 8% of a composition consisting essentially of methylolstearamide and, as the dispersing agent therefor, dodecylphenoxyethoxymethyl pyridinium chloride, the ratio of said methylolstearamide to said pyridinium chloride being from 1:1 to 2:1, drying the impregnated material, and heating to a temperature from 120 to 250° C. for a period ranging from 10 minutes to 45 seconds.



14. A process for rendering textile materials water-repellent, which comprises impregnating the textile material with an aqueous dispersion containing 3 to 8% of a composition consisting essentially of methylolstearamide and, as the dispersing agent therefor, β-stearoyloxyethoxymethyl pyridinium chloride, the ratio of said methylolstearamide to said pyridinium chloride being from 1:1 to 2:1, drying the impregnated material, and heating to a temperature from 120 to 250° C. for a period ranging from 10 minutes to 45 seconds

15. A process for rendering textile materials water-repellent, which comprises impregnating the textile material with an aqueous dispersion containing 3 to 8% of a composition consisting essentially of methylolstearamide and, as the dispersion agent therefor, stearoylamidomethyl triethyl ammonium triethylamine sulfite, the ratio of said methylolstearamide to said quaternary ammonium sulfite being from 1:1 to 2:1, drying the impregnated material, and heating to a temperature from 120 to 250° C. for a period ranging from 10 minutes to 45 seconds.

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