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GREASE WHEREIN THE THICKENER COMPRISES METAL SOAPS OF HYDROXY FATTY ACID FORMALS

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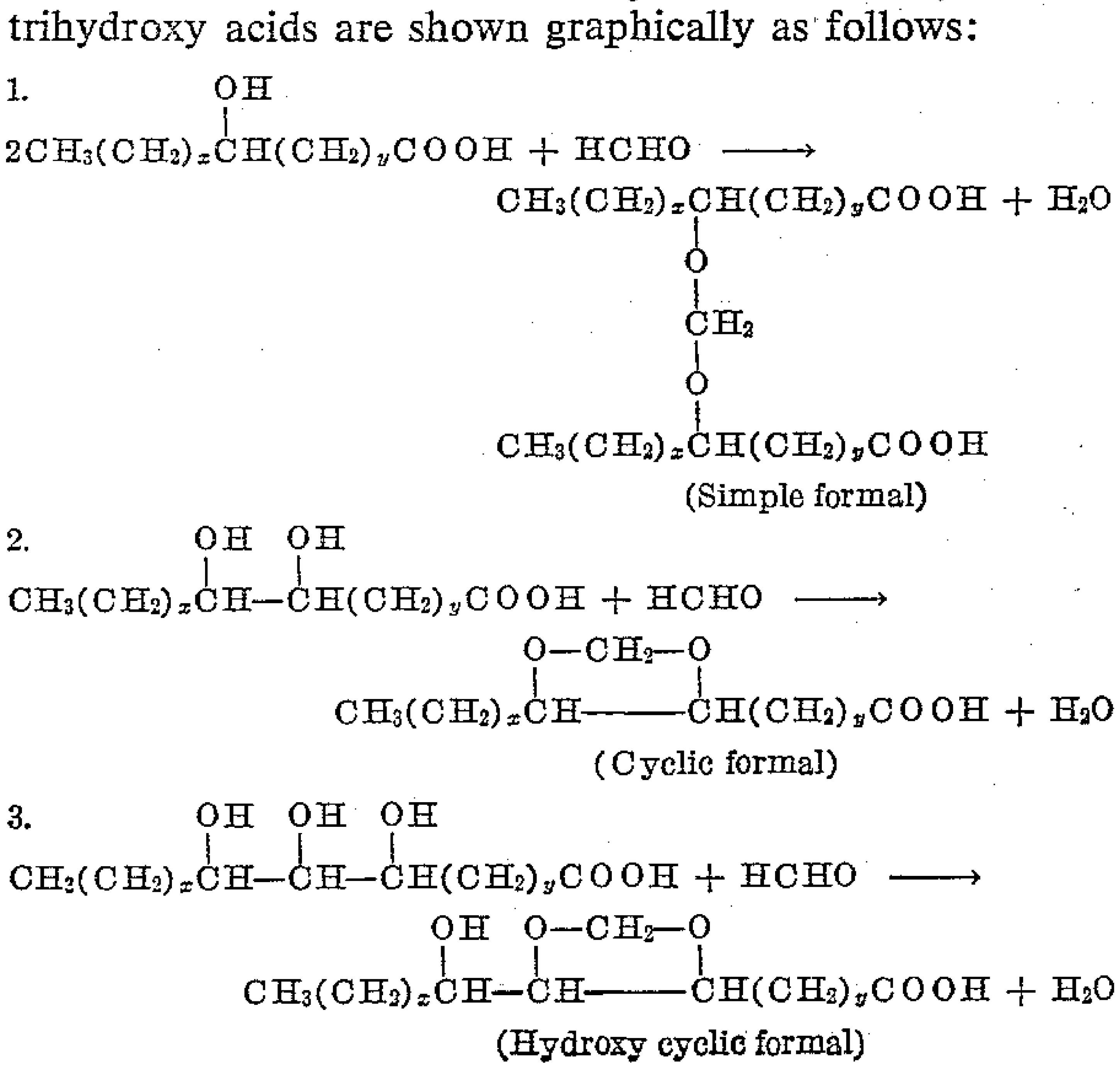
This invention relates to lubricating grease compositions. Particularly, the invention relates to lubricating grease compositions prepared by thickening a lubricating oil to a grease consistency with metallic soaps of formals of hydroxy fatty acids. The products are excellent grease compositions having outstanding structural stability and long lubricating life.

There have recently become available new hydroxy fatty acids produced from unsaturated fatty acids by treatment with oxidation agents. For example, unsaturated acids having from about 14 to about 22 carbon atoms such as tetradecenoic acids, e. g., myristoleic acid, tsuzuic acid, hexadecenoic acids, e. g., palmitoleic acid, octadecenoic acids, e. g., petroselenic acid, oleic acid, elaidic acid, vaccenic acid, eicosenoic acids, e. g., gadoleic acid, docosenoic acids, e. g., erucic acid, cetoleic acid, mixtures of the above, and the like, are oxidized with peracetic acid, resulting in polyhydroxy acids such as di-hydroxy stearic acid, etc. These new hydroxy fatty acids are considerably less expensive than the hydroxy fatty acids available heretofore, which have ordinarily been formed by the hydrogenation of castor oil. Naturally occurring hydroxy fatty acids, and mixtures, such as ricinoleic acid, 12 hydroxy stearic acid, sabinic acid (12-hydroxy lauric acid), juniperic acid (16 hydroxy palmitic acid) are also available commercially.

It has now been found that greases of excellent properties can be prepared using derivatives of these hydroxy fatty acids in the formulation. In these modifications, the mono- and polyhydroxy fatty acids are reacted with formaldehyde to form (1) the simple di-acid formal from the monohydric acid, (2) the cyclic formal in the case of a dihydroxy fatty acid and (3) the hydroxy cyclic formal in the case of a trihydroxy acid.

These reactions of formaldehyde with mono-, di- and trihydroxy acids are shown graphically as follows:



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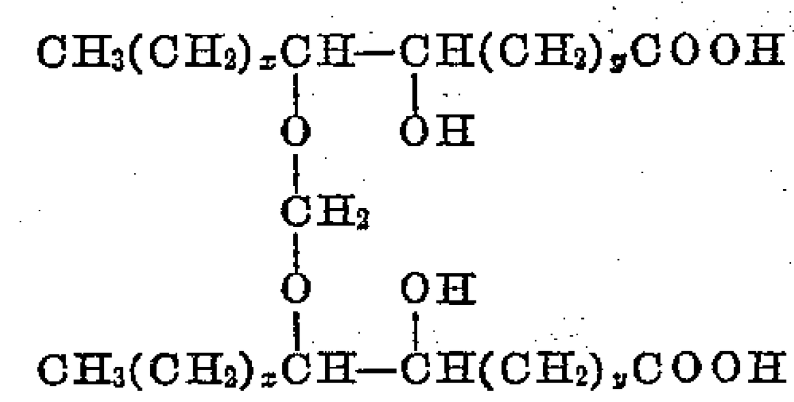
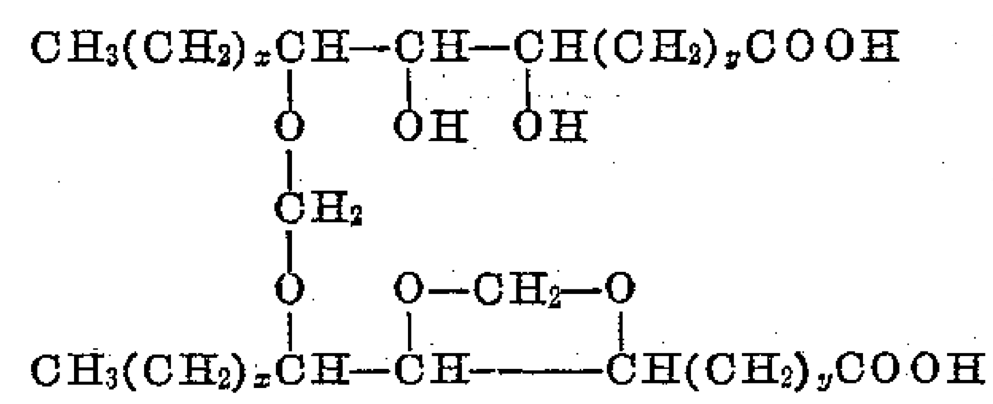
In addition to the above, mixed products could be formed. For example, the dihydroxy fatty acid could react with formaldehyde to form dihydroxy di-acid formals such as



while the trihydroxy fatty acid could react with formaldehyde to form formals containing free hydroxy groups and/or cyclic formal groups such as



The exact position of the hydroxy groups and of the simple and complex formal linkages are not definitely established.

These formals of hydroxy fatty acids have been found to be excellent soap forming materials suitable as grease thickeners, as is pointed out in the examples below. The hydroxy fatty acid mixture alone, however, results in a composition which is too soft for most purposes.

EXAMPLE I.—SIMPLE SOAP GREASE USING A POLYHYDRIC FATTY ACID ALONE

Formulation

Polyhydroxy stearic acid	12.00
Lithium monohydrate	1.72
Phenyl alpha-naphthylamine	0.50
Mineral oil	85.78

Preparation

Charged mineral oil and acid to a fire heated grease kettle and warmed to 150° F. Then added the

$$LiOH \cdot H_2O$$

as a 20% aqueous solution and heated to 400° F. Added phenyl alpha-naphthylamine and allowed to cool; when cold, homogenized.

Penetrations, 77° F., mm./10:

Unworked	290.
Worked 60 strokes	350.
Worked 100,000 strokes	Fluidized.

No further work, due to poor structural stability of grease.

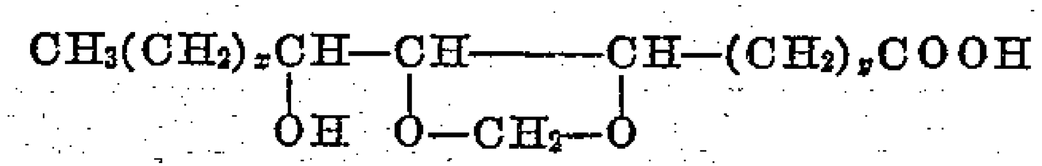
EXAMPLE II.—FORMAL OF POLYHYDROXY ACID IN SIMPLE SOAP GREASE

The polyhydroxy acid used to prepare the formal of this example was obtained by the peroxidation of oleic acid. The polyhydroxy fatty acid had the following physical and chemical properties:

Gardner color		16
Volatile matter	percent	0.7
Melting point	° C.	60–64
Acid value		170
Iodine value		4
Sap. value		181
Hydroxyl value		270

Formulation and preparation

Same as above, employing



Penetration (77° F.—mm./10):

Unworked	255
Worked 60 strokes	265
Worked 10,000 strokes	285

EXAMPLE III.—FORMAL OF MONOHYDROXY FATTY ACID IN A COMPLEX GREASE

Formulation

	Percent weight
Formal of mono hydroxy stearic acid	4.0
Glacial acetic acid	8.0
Hydrated lime	6.0
Phenyl alpha-naphthylamine	0.5
Mineral oil (55 SUS/210° F.)	81.5

Preparation

Charged formal, hydrated lime and mineral oil to a fire heated kettle and warmed to 150° F. Then added acetic acid and continued heating to 500° F. Discontinued heating and cooled to 250° F. Added phenyl alpha-naphthylamine and cooled further to 200° F. Gaulin homogenized the product at 3000 p. s. i. pressure, filtered and packaged.

EXAMPLE IV

Formulation

	Percent weight
Formal of mono hydroxy stearic acid	2.0
Hydrofol acid 51	2.0
Glacial acetic acid	8.0
Hydrated lime	6.0
Phenyl alpha-naphthylamine	0.5
Mineral oil (55 SUS/210° F.)	81.5

Preparation

Similar to Example I.

Properties	Example III	Example IV
Appearance	Excellent	Excellent.
Penetrations (77° F. mm./10):		
Unworked	255	250.
Worked, 60 strokes	330	271.
Worked, 100,000 strokes	Semi-fluid	368.
Dropping point, ° F	None	None.
Phase changes (70–500° F.)	do	Do.
Wheel bearing test 6 hours at 220° F., 660 R. P. M.	Pass	Pass.
Norma-Hoffman oxidation, hours to 5 p. s. i. drop.	302	302.
Water solubility (boiling water)	None	None.

EXAMPLE V.—FORMAL OF DI-HYDROXY STEARIC ACID IN COMPLEX GREASE

The di-hydroxy stearic acid used in this example had the following properties:

Gardner color	10
Volatile matter (percent)	0.8
Melting point, °C	80–83
Acid value	168
Iodine value	3
Sap. value	182
Hydroxyl value	257

The hydroxy stearic acid (95 g., 0.3 m.) was heated with 9 g. of paraformaldehyde, 0.3 g. $NaHSO_4$ catalyst, and 100 g. heptane to a reflux temperature of 103° F. for 1½ hours. During this time 6.2 cc. of water was azeotroped from the reaction mixture (theory is about 6 cc.). The material was then cooled, filtered to remove the catalyst and stripped to remove the heptane (120° C. at 10 mm.). The liquid formal product was used to make a grease as follows:

Formulation

Ingredients:	Percent weight
Hydrogenated fish oil acids	2.0
Cyclic formal of dihydroxy stearic acid	2.0
Glacial acetic acid	8.0
Hydrated lime	6.0
Phenyl alpha-naphthylamine	0.5
Mineral oil (55 SSU/210° F.)	81.5

Preparation

The mineral oil, lime and high molecular weight acids were charged to a fire heated kettle and warmed to 135° F. The acetic acid was added and heating continued to 500° F. Shut off heat and while continuing to agitate, cooled to 250° F. when the phenyl alpha-naphthylamine was added. Cooled to 200° F., then homogenized, filtered and packaged.

Properties:

Appearance	Excellent, short fibre grease.
Dropping point, °F	None.
Penetrations, 77° F. mm./10:	
Unworked	210.
Worked 60 strokes	265.
Worked 100,000 strokes	205 (110° F.), 277 after cooling and working additional 60 strokes.
Water solubility	Nil.
Norma-Hoffman oxidation, hours to 5 p. s. i. drop in oxygen pressure	310.
Wheel bearing test (6 hours at 250° F.)	Pass, no leakage.
Phase changes	None, up to 450° F.

EXAMPLE VI.—FORMAL OF POLYHYDROXY STEARIC ACID IN COMPLEX GREASE

Polyhydroxy stearic acid, 165.5 g. (0.5 m.), was formalized with 8.2 g. paraformaldehyde in the presence of 0.5 $NaHSO_4$ catalyst and 100 g. heptane for 2 hours at 107° C. The water collected was 7.4 cc. (theory is 9 cc.). This material consisting of a mixture of simple and cyclic formals was filtered while hot and then stripped free of heptane (120° C. at 15 mm.). It had some free hydroxyl groups still remaining and was a mushy material which on standing solidified. It was used to prepare a grease as follows.

Formulation

Ingredients:	Percent weight
Hydrogenated fish oil acids	2.0
Polyhydroxystearic acid mono formal	2.0
Glacial acetic acid	8.0
Hydrated lime	6.0
Phenyl alpha-naphthylamine	0.5
Mineral oil (55 SSU/210° F.)	81.5

Preparation

Same as Example V.

Properties:

Appearance	Excellent, smooth homogeneous product.
Dropping point, °F	None.
Penetration 77° F. mm./10:	
Unworked	210.
Worked 60 strokes	228.
Worked 100,000 strokes	316.
Water solubility	Insoluble.

Phase changes	None up to 450° F.
Wheel bearing test, 6 hours at 220° F.	Pass, no leakage.
Norma-Hoffman oxidation, hours to 5 p. s. i. drop	375.
Lubrication life hours, 10,000 R. P. M.—250° F.	1166.

It will be seen by the data in the examples above that the formals of hydroxy fatty acids make excellent grease soaps, giving lubricating grease compositions having very satisfactory performance characteristics. As is shown in Example I, the polyhydroxy acids alone do not form satisfactory grease compositions in that they tend to over-plasticize the grease and give products that are too soft to perform satisfactory lubricating functions.

In addition to the metals used in the example above, the formals of the hydroxy fatty acids may be saponified with any of the commonly known alkali or alkaline earth metals to form satisfactory grease soaps. The choice of the metal component depends to a certain extent on the use for which the soap is contemplated. The alkaline earth metals, particularly calcium, strontium, barium and magnesium, may be used and the alkali metals such as sodium, lithium and potassium may also be used in certain formulations. The alkaline earth metals are particularly advantageous for use in preparing the high acetate complex grease structures. As is pointed out above, in addition to the formal of the hydroxy fatty acids, other soap forming acidic materials may be incorporated into the grease compositions of invention. Any of the commonly known high molecular weight acids having from about 12 to about 30 carbon atoms, preferably those having from 14 to 22 carbon atoms, may be used. These acids may be derived from saturated or unsaturated, naturally occurring or synthetic fatty materials. Examples of operable fatty acids include stearic, arachidic, hydrogenated fish oil acids, coconut oil acids, tallow acids, etc.

When it is desired to prepare a complex lubricating grease, the high molecular weight portion of the total soap content is complexed with a low molecular weight acid salt. Such low molecular weight acids include those having from about 1 to about 6 carbon atoms, such as formic, acetic, propionic, and similar acids, including their hydroxy derivatives such as lactic acid, etc. The amount of the low molecular weight acid salt that is used to form the complex with the high molecular weight fatty acid will again depend upon the use for which the grease composition is desired. It has recently been found that grease compositions containing a high ratio of low molecular weight acid to high molecular weight acid are particularly outstanding for high temperature use. Especially desirable grease compositions may be prepared by thickening to a grease consistency a lubricating oil with a complex alkaline earth soap grease wherein the complex soap comprises a mixture of high molecular weight acid salt in a mol ratio of salt to soap of between about 7.5:1 to 50:1, preferably 9:1 to 15:1.

The total amount of the soap used in preparing the grease formulations will vary from between about 3 to about 30 weight %, based on the weight of the total composition. Within this broad range, from about 6% to about 20% will normally be found to be preferable. The choice of the menstruum used in preparing the lubricating greases of invention may be made from a wide range of lubricating oils, whether naturally occurring or synthetic. Quite generally this oil should have a viscosity within the range of about 35 to about 200 SUS at 210° F. and flash points of about 350° to about 600° F. Among the synthetic lubricants operable may be mentioned diesters of dibasic acids, complex esters, formals, hydrocarbon polymers, silicone oils, polyglycol derivatives, etc. The naturally occurring lubricating oils used

may be either of naphthenic or paraffinic origin refined by any of the techniques well known to the art.

When it is desired to utilize the formals of the hydroxy fatty acids in conjunction with another high molecular weight fatty acid, the two soap forming materials may be admixed in any desired proportion. In other words, the soap may consist entirely of the metallic soap of the formal of the hydroxy fatty acid, or relatively minor amounts, that is from about 1% to about 10%, of the total high molecular weight acid.

Any of the commonly known grease additive materials such as stabilizers, oxidation inhibitors, cooling agents, tackiness agents or the like may be blended with the grease compositions of this invention.

To summarize briefly, the instant invention relates to new and improved lubricating grease compositions which are prepared by thickening a lubricating oil base stock to a grease consistency with a minor but grease forming amount of a metal soap of a formal of a hydroxy fatty acid. The hydroxy fatty acid may be a mono hydroxy material or it may be a polyhydroxy fatty acid. Other grease making fatty acid soaps may be combined with the formals and the total grease making soap composiion may be complexed with low molecular weight acids such as formic acid, acetic acid, furoic acid and the like. Normally from 5% to 30% by weight of the total grease thickener will be used, preferably about 6 weight percent to about 20 weight percent. When a complex grease composition is contemplated, the low molecular weight acid used to form the complex may be present in amounts varying between about 3 to about 20 weight percent of the total composition. Especially preferred are the complex grease compositions comprising a low molecular weight acid having from 1 to 6 carbon atoms with high molecular weight acids having from 12 to 30 carbon atoms in a mol ratio of low molecular weight acid to high molecular weight acid of from 7.5:1 to 20:1.

What is claimed is:

1. A lubricating grease composition comprising a mineral lubricating oil containing combined therein a minor, but grease thickening, amount of metal soap of a formal of a hydroxy-fatty acid having from about 14 to 22 carbon atoms, said metal constituent being selected from the group consisting of alkali and alkaline earth metals.

2. A lubricating grease composition which comprises a lubricating oil base stock thickened to a grease consistency with a complex soap which comprises a metal salt of a low molecular weight acid, a metal soap of a high molecular weight fatty acid and a metal soap of a formal of a hydroxy-stearic acid, said metal constituents being selected from the group consisting of alkali and alkaline earth metals.

3. A lubricating grease composition according to claim 2 wherein said metal soap and wherein said metal salt are of calcium.

4. A lubricating grease composition according to claim 2 wherein said hydroxy-stearic acid is a mono-hydroxy-stearic acid.

5. A lubricating grease composition according to claim 2 wherein said hydroxy-stearic acid contains more than one hydroxy group.

6. A lubricating grease composition comprising a major proportion of a lubricating oil and a minor, but grease thickening, amount of a soap-salt complex which comprises the alkaline earth metal soap of a mixture of a high molecular weight fatty acid and a formal of a hydroxy-stearic acid and the alkaline earth metal salt of a low molecular weight acid containing from 2 to 6 carbon atoms, the molar ratio of said salt to said mixture of soaps in said complex being between about 7.5:1 to 20:1, and wherein said mixture consists of about equal weight percentages of said high molecular weight fatty acid and said formal.

7. A lubricating grease composition comprising a lubricating oil thickened to a grease consistency with a metal

soap-salt complex, which consists of a metal salt of a low molecular weight fatty acid and a metal soap of a formal of a hydroxy fatty acid having from about 14 to 22 carbon atoms, said metal constituents being selected from the group consisting of alkali and alkaline earth metals and wherein the molar ratio of said salt to said soap is about 7.5:1 to 20:1.

8. The lubricating grease composition of claim 7 wherein said metal salt is acetic acid.

9. The lubricating grease composition of claim 7 wherein said hydroxy fatty acid is mono-hydroxy stearic acid.

References Cited in the file of this patent

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