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EMULSIONS

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14 Claims. (Cl. 167—90)

This invention relates to the preparation of emulsions or dispersions containing aqueous and oleaginous materials and compositions therefor, and is particularly concerned with the preparation of cosmetic preparations in the form of emulsions of oleaginous and aqueous materials, particularly emulsions having a pH of about 7 and especially those having a pH below 7.

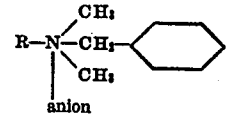
Emulsions or dispersions of the character referred to have heretofore been prepared in which emulsifying or dispersing agents, or combinattions thereof, of numerous types, have been utilized. While the stability of these emulsions or dispersions is enhanced by the addition of said emulsifying or dispersing agents or combinations thereof, still, in many instances, the improvements have not been sufficiently marked so as to provide a completely satisfactory solution to the problems confronting those versed in the art.

Among the numerous emulsifying or dispersing agents whose use has been suggested for enhancing the stability of oleaginous-aqueous emulsions are the higher molecular weight aliphatic alcohol sulphates and sulphonates, the sulphonated oils such as Turkey-Red oil, the sulphates and phosphates of higher fatty acid monoglycerides, monoglycerides and diglycerides of higher molecular weight aliphatic, particularly, fatty acids, and the like. It has also been proposed to utilize mixtures of higher fatty acid monoglycerides or the like with salts of sulphonic acid derivatives or sulphuric acid esters of higher molecular weight aliphatic alcohols, as, for example, combinations of monolaurin with lauryl sodium sulphate and the like. It has been proposed also to employ combinations of monoglycerides or other partially esterified polyhydric alcohols together with fatty acid amino products resulting from reacting higher molecular weight fatty acid acyl halides with protein decomposition products. Furthermore, the suggestion has been made to utilize, as emulsifying agents for aqueous-oleaginous emulsions, mixtures of agents one of which contains a colloidal cation and the other a colloidal anion. In none of the cases have the agents which have been proposed to be used been found fully satisfactory.

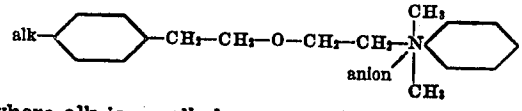
In accordance with the present invention, emulsions or dispersions of excellent character and stability, particularly cosmetic emulsions, are produced by utilizing a combination of certain agents, hereinafter defined and described in detail. These agents comprise an intimate mixture of (1) certain cation-active substances and (2) non-ionic substances, the non-ionic substances substantially predominating in amount over the cation-active substance at least in most cases.

The cation-active substances may be of aliphatic, carbocyclic, or heterocyclic character and, as will be understood, comprise substances in which the surface activity is due to a group or radical present in the cationic portion of the molecule. Among the cation-active compounds which may be employed in accordance with the present invention are the bases or their salts, such as may be derived from pentavalent nitrogen, and further the sulphonium, phosphonium and arsonium, etc., bases and their salts. The quaternary ammonium compounds are examples of especially satisfactory compounds, the pyridonium or pyridinium compounds being specific examples thereof. In the bases or their salts, the innocuous anions may be hydroxide, chloride, sulphate, bromide, iodide, acetate, tartrate, sulphite, etc. The groups inducing cation activity comprise long chain groupings such as aliphatic hydrocarbon chains having at least six and preferably from twelve to eighteen carbon atoms. The long chain groupings may be composed of two or more benzene nuclei or other cyclic radicals, either combined directly or, for example, through carbon or nitrogen or other linkages, with or without aliphatic chains substituted for the hydrogen in rings.

Examples of cation-active substances which may be used in accordance with our invention include octyl pyridinium iodide; dodecyl pyridinium bromide; hexodecyl pyridinium iodide; octadecyl pyridinium bromide; dodecyl pyridinium iodide; dodecyl pyridinium chloride; dodecyl-triethyl ammonium iodide; cetyl trimethyl ammonium chloride, bromide or iodide; octyl-triethyl ammonium iodide; decyl-triethyl ammonium iodide; dodecyl-triethyl ammonium iodide; hexadecyl-triethyl ammonium iodide;

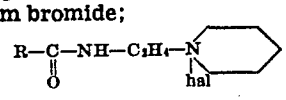


where R is alkyl or mixtures of alkyls containing at least 8 C and particularly from 12 to 16 C, the anion being preferably Cl, Br, or I; salts of higher molecular weight aliphatic straight chain and branched chain amines such as octyl amine hydrochloride; lauryl amine hydrochloride; myristyl amine hydrochloride; cetyl amine hydrochloride; oleyl amine acetate; stearyl amine hydrochloride; dioctyl amine hydrochloride; didodecyl amine acetate or hydrochloride; and the like;

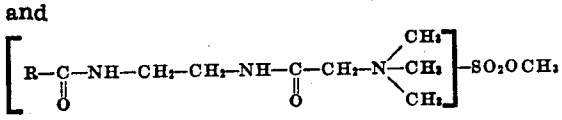


where alk is an alkyl group containing at least 8 C and particularly from 12 to 16 C, the anion being preferably Cl, Br or I; toluene azophenyl-tri-

methyl ammonium iodide; benzene azophenyl-trimethyl-ammonium iodide; diphenyl-azophenyl-trimethylammonium methyl-sulphate; isopropyl-naphthyl-trimethyl ammonium iodide; diethyl-dodecyl sulphonium hydroxide; triethyl-dodecyl phosphonium hydroxide; trimethyl dodecyl phosphonium iodide; trimethyl-dodecyl phosphonium bromide;



and

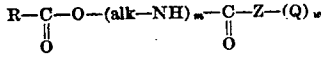


where hal is Cl, Br or I, and

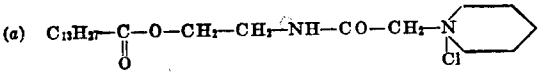


is the acyl radical of an aliphatic, particularly fatty, acid containing at least 8 C and particularly from 12 to 16 C.

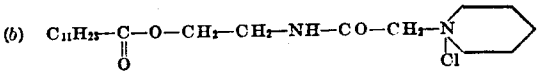
An especially useful group of cation-active substances for the purposes of the present invention are the compounds which correspond to the formula



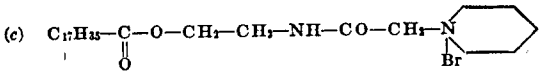
where R is a hydrocarbon radical or substituted hydrocarbon radical containing at least seven and preferably from eleven to seventeen carbon atoms, alk stands for hydrocarbon, for example, alkylene or arylene such as ethylene or phenylene, Z is a hydrocarbon radical, Q is a quaternary ammonium radical, and *m* and *w* are whole numbers, *w* being preferably 1 or 2. Representative of such compounds are the following:



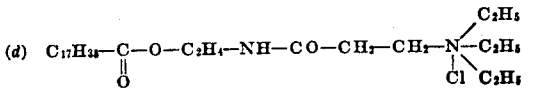
(a)



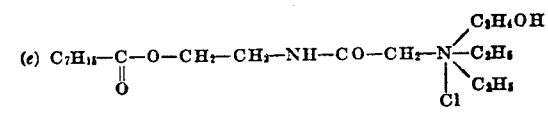
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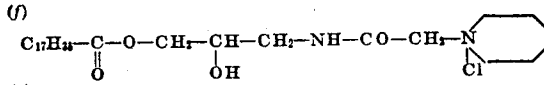


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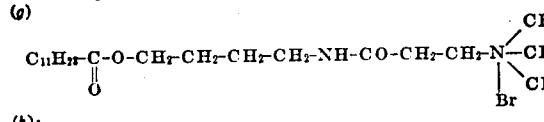


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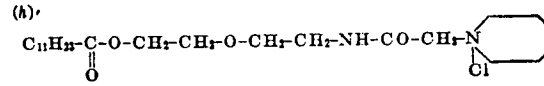
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(g)

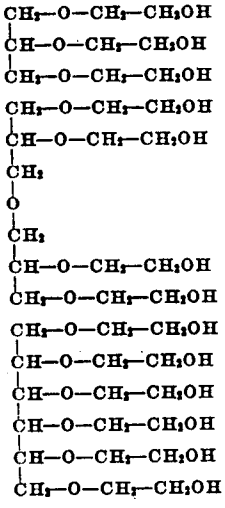


(h)



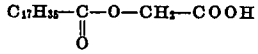
The non-ionic substances are, in general, derivatives of aliphatic alcohols containing at least one free hydroxy group, particularly aliphatic polyhydroxy substances or polyhydric alcohols incompletely esterified with higher molecular weight aliphatic (including cycloaliphatic) acids, particularly, fatty acids. Higher alkyl partial ethers of the aliphatic polyhydroxy substances may be used instead of the esters but, in general, they are not nearly so satisfactory although their use is within the broader aspects of the invention. Representative examples of such non-ionic substances are, for example, higher molecular weight fatty acid monoglycerides such as monocaprylin, monolaurin, monostearin, mono-olein, mono-palmitin; higher molecular weight fatty acid mono-esters of polyglycerols, glycols and polyglycols such as the stearic acid mono-ester of diglycerol, the oleic acid mono-ester of ethylene glycol, the oleic mono-ester of diethylene glycol; amides containing at least one free hydroxy group as, for example, lauric acid amide of diethanolamine, lauric and myristic acid amides of hydroxy-ethyl ethylene diamine; alkyl partial ethers such as lauryl mono-ether of glycerol, myristyl mono-ether of diethylene glycol, decyl mono-ether or diglycerol, hexyl di-ether of glycerol, lauryl di-ether of diglycerol, cetyl mono-ether of glycerol, oleyl mono-ether of sorbitol, stearyl mono-ether of mannitol, and the like.

Among the aliphatic polyhydroxy substances whose partial esters comprise the non-ionic agents which are used in combination with the aforementioned cation-active substances, are, for example, including some previously mentioned, glycerol; glycols such as ethylene glycol, propylene glycol, trimethylene glycol, butylene glycol and higher homologues or long chain glycols; polyglycols such as diethylene glycol, triethylene glycol, pentaethylene glycol, hexamethylene glycol, and the higher homologues such as "Carbowax"; pentaerythritol; quercitol; dihydroxy acetone, polyglycerols such as diglycerol, triglycerol, tetraglycerol and the like including mixtures thereof; carbohydrates or sugars including mono-, di- and polysaccharides such as dextrose, sucrose, xylose, arabinose, galactose, fructose, maltose, mannose, dextrin, starch, and the like; sugar alcohols such as arabitol, mannitol, sorbitol, dulcitol, arabitan, mannitan, sorbitan, mannide, and sorbide; and polyhydroxycarboxylic acids such as tartaric acid, mucic acid, saccharic acid, gluconic acid, glucuronic acid, gulonic acid, mannonic acid, trihydroxyglutaric acid, glyceric acid, carboxylic oxidation products of polyglycerols, others of similar character, and hydroxyethyl and hydroxypropyl ether derivatives of the above, as, for example:



(For convenience, all hydroxy groups are written facing one way.)

The higher molecular weight carboxylic aliphatic acids which are esterified with the aforementioned or similar aliphatic polyhydroxy substances to form the non-ionic agents which are used in accordance with the present invention may be selected from a large group including, among those mentioned, straight chain and branched chain, saturated and unsaturated, carboxylic, aliphatic (including cycloaliphatic), fatty, such as caprylic acid, caproic acid, capric acid, pimelic acid, sebacic acid, behenic acid, arachidic acid, cerotic acid, erucic acid, melissic acid, stearic acid, oleic acid, ricinoleic acid, ricinelaidic acid, ricinostearolic acid, linoleic acid, linolenic acid, lauric acid, myristic acid, palmitic acid, mixtures of any two or more of the above-mentioned acids or other acids, mixed higher fatty acids derived from animal or vegetable sources, for example, lard, coconut oil, rapeseed oil, sesame oil, palm kernel oil, palm oil, olive oil, corn oil, cottonseed oil, sardine oil, tallow, soya bean oil, peanut oil, castor oil, seal oils, whale oil, shark oil and other fish oils, partially or completely hydrogenated animal and vegetable oils such as those mentioned; oxidized and/or polymerized higher fatty acids or higher fatty acids derived from oxidized and/or polymerized triglyceride oils; acyloxy carboxylic acids such as



hydroxy and alpha-hydroxy higher carboxylic, aliphatic and fatty acids such as i-hydroxy stearic acid, dihydroxypalmitic acid, dihydroxystearic acid, dihydroxybehenic acid, alpha-hydroxy capric acid, alpha-hydroxy stearic acid, alpha-hydroxy palmitic acid, alpha-hydroxy lauric acid, alpha-hydroxy myristic acid, alpha-hydroxy coconut oil mixed fatty acids, alpha-hydroxy margaric acid, alpha-hydroxy arachidic acid, and the like; fatty and similar acids derived from various waxes such as beeswax, spermaceti, montan wax, coccerin, and carnauba wax and higher molecular weight carboxylic acids derived, by oxidation and other methods, from paraffin wax, petroleum and similar hydrocarbons.

The following examples are illustrative of the preparation of combinations of cation-active substances and non-ionic agents which may be employed in accordance with the present invention. It will be appreciated that the proportions thereof may be varied, that various mixtures of different agents or substances of the two types may be employed and that other modifications and variations may be made without departing from the guiding principles which are disclosed herein:

Example 1

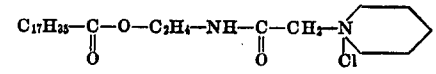
250 grams of a mixture of monostearin and distearin and 50 grams of lauryl amine hydrochloride were mixed together at 100 degrees C. and the mass was then permitted to cool.

Example 2

90 grams of monostearin containing some distearin were heated to 100 degrees C. and were mixed with 10 grams of lauryl pyridinium iodide. At 80 degrees C., the product was a clear yellow liquid, cooling to a waxy solid at room temperature.

Example 3

45 grams of the stearic acid mono-ester of diethylene glycol and 5 grams of a compound having the following formula



were heated together at approximately 100 degrees C. until a clear solution was obtained. The mass was then allowed to cool.

Example 4

90 grams of monostearin containing some distearin were heated to 125 degrees C. and mixed with 10 grams of cetyl pyridinium chloride and the mass was then permitted to cool.

Example 5

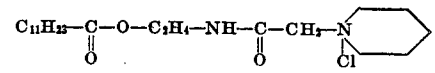
80 grams of monostearin containing some distearin were heated to 120 degrees C. and mixed with 20 grams of cetyl trimethyl ammonium chloride and the mixture was permitted to cool.

Example 6

90 grams of monostearin containing some distearin were heated to 125 degrees C. and mixed with 10 grams of cetyl pyridinium iodide until a clear solution was obtained. The mass was then permitted to cool.

Example 7

85 grams of the stearic acid mono-ester of diethylene or triethylene glycol (containing a small proportion of the diester) and 15 grams of a compound having the formula



were heated together at about 100 degrees C. until a clear solution was obtained and then the mass was allowed to cool.

The oleaginous-aqueous emulsions or dispersions in which the combination of cation-active substances and non-ionic agent are incorporated may be, in general, of varying character, but especially satisfactory results have been obtained in connection with acid-reacting emulsions, particularly cosmetic emulsions of this type. A noteworthy example of the type of cosmetic emulsions to which the present invention relates is cosmetic astringent creams. In general, such creams contain, in addition to oleaginous and aqueous constituents, a salt of a strong acid with a polyvalent metal, such as aluminum chloride and aluminum sulphate. Although, as stated, the invention is especially concerned with cosmetic emulsions of the character indicated, it will be appreciated that the invention is not so limited. Emulsions or dispersions containing oleaginous materials and aqueous materials, and particularly those having an acid reaction, to which the principles of the present invention may be adapted include also medicinal and pharmaceutical emulsions, furniture polishes, automobile polishes, certain resin emulsions, and the like.

The following examples are representative of types of emulsions which may be made in accordance with the principles of the present invention:

Example A

20 grams of the product of Example 2 and 10 grams of light mineral oil were heated to 60 degrees C., with stirring, and there were then stirred thereinto 15 grams of hydrated aluminum

chloride dissolved in 55 cc. of water, the aluminum chloride solution having previously been heated to approximately 60 degrees C. The mixture was stirred until it had cooled to room temperature.

Example B

(1) 42 grams of the product of Example 4, 14 grams of spermaceti, 4 grams of glycerine, and 60 cc. of water were mixed together and brought to a boil, with stirring, until a uniform emulsion or dispersion was obtained. The emulsion was then permitted to cool to about 50 degrees C.

(2) A solution was made by heating a mixture, to about 60 degrees C., of 20 grams of $AlCl_3.6H_2O$, 20 grams of $Al_2(SO_4)_3.18H_2O$, and 40 cc. of water. It was allowed to cool to about 50 degrees C.

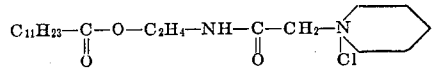
(3) The solution produced in part (2) hereof was then added slowly and with constant stirring to the emulsion of part (1) hereof. A medium viscous white emulsion resulted which, on standing several hours, set to a firm cream having excellent smoothness and texture. The cream was highly satisfactory as an anti-perspirant.

Example C

15 grams of the product of Example 5 were melted together with 80 grams of paraffin wax having a melting point of 138 degrees F. to 140 degrees F. The mixture was heated to about 100 degrees C. and the same was added slowly and with constant stirring to 105 cc. of water also maintained at about 100 degrees C. The mixture was stirred constantly during the addition and until the mass had reached room temperature. The product comprised a fine dispersion of wax which could be diluted with water. The resulting product was very satisfactory for the coating and impregnating of paper stock.

Example D

20 grams of a mixture of the stearic acid mono-ester of diethyleneglycol (containing a small proportion of the diester) and a compound having the following formula



(the stearic acid mono-ester of diethyleneglycol comprising 90% of said mixture), were melted and mixed with 30 grams of light mineral oil, the mixture being heated to 80 degrees C. Said mixture was then added slowly and with constant stirring to a solution containing 45 cc. of water and 5 grams of glacial acetic acid, said solution also being maintained at about 80 degrees C. The mixture was constantly stirred until room temperature was reached. The product was a white, viscous emulsion at room temperature and was useful as a furniture polish.

Example E

10 grams of the product of Example 3, 40 grams of light mineral oil and 5 grams of spermaceti were heated together to 80 degrees C. whereupon a clear oleaginous solution was formed. The same was then added slowly and with constant stirring to a solution containing 40 cc. of water and 5 grams of tartaric acid, said solution also being at 80 degrees C. The mass was constantly stirred during the addition and the stirring was continued until the resulting emulsion reached room temperature. The product, which was a heavy, white emulsion, was very useful as a cosmetic cream.

The proportions of the cation-active substance and non-ionic agent employed in the emulsions or dispersions are subject to relatively wide variations, the amount utilized being dependent, among other things, upon the potency of the substances or agents selected, the specific character of the emulsions with which they are utilized, and the exact results desired. In general, from about 0.1% to 5.0%, based upon the weight of the oleaginous constituent or constituents, is effective for most purposes but the amount may be increased substantially.

It will be understood that the term "oleaginous," as used in the claims, is intended to include water-repellent or hydrophobic substances such as oils and fats of animal, vegetable and mineral origin; waxes such as paraffin, carnauba wax, beeswax, montan wax, candelilla wax, and the like; higher molecular weight fatty acids such as stearic acid, palmitic acid, and the like; completely esterified polyhydroxy substances such as tristearin, higher fatty acid di-esters of glycols and polyglycols, and the like; lanolin or wool grease, and numerous other materials of the character indicated.

The term "higher," as used in the claims to refer to fatty acids, amines and the like, will be understood to mean at least six carbon atoms unless otherwise expressly stated.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. An emulsion containing an oleaginous material, an aqueous material, and small proportions of (1) a cation-active substance in the form of a pyridinium halide having directly attached to the nitrogen thereof a hydrocarbon radical containing at least 8 carbon atoms, and (2) a non-ionic substance in the form of a carboxylic acid derivative of an aliphatic hydroxy compound, the carboxylic acid radical of which contains at least 8 carbon atoms, said derivative containing at least one unesterified hydroxy group in the radical of the aliphatic hydroxy compound.

2. A cosmetic astringent cream containing oleaginous material, aqueous material, an astringent substance, and small proportions of (1) a cation-active substance in the form of a pyridinium halide having directly attached to the nitrogen thereof a hydrocarbon radical containing at least 8 carbon atoms, and (2) an aliphatic polyhydroxy substance incompletely esterified with a higher molecular weight fatty acid.

3. A cosmetic emulsion containing an oleaginous material, an aqueous material, and small proportions of (1) a cation-active substance in the form of a pyridinium halide having directly attached to the nitrogen thereof a hydrocarbon radical containing at least 8 carbon atoms, and (2) glycerol incompletely esterified with a higher molecular weight fatty acid.

4. A cosmetic astringent cream containing oleaginous material, aqueous material, an astringent substance in the form of an aluminum salt of a mineral acid, and small proportions of (1) a cation-active substance in the form of a pyridinium halide having directly attached to the nitrogen thereof a hydrocarbon radical containing at least 8 carbon atoms, and (2) glycerol incompletely esterified with a higher molecular weight fatty acid.

5. A non-alkaline emulsion containing an oleaginous material, an aqueous material, and small proportions of (1) an aliphatic polyhydroxy substance incompletely esterified with a fatty acid containing from 12 to 18 carbon atoms, and

(2) a cation-active pyridinium halide having directly attached to the nitrogen thereof a hydrocarbon radical containing at least 8 carbon atoms.

6. A cosmetic emulsion containing an oleaginous material, an aqueous material, and small proportions of (1) a cation-active substance comprising a quaternary-ammonium halide in which a hydrocarbon radical containing at least 8 carbon atoms is directly attached to the nitrogen atom, and (2) glycerol partially esterified with a higher molecular weight fatty acid.

7. An emulsion containing an oleaginous material, an aqueous material, and small proportions of (1) an aliphatic polyhydroxy substance incompletely esterified with a higher molecular weight fatty acid, and (2) a cation-active quaternary ammonium compound in which an aliphatic hydrocarbon radical containing at least 8 carbon atoms is directly attached to the nitrogen atom.

8. An emulsion containing oleaginous material, aqueous material, and small proportions of (1) an aliphatic polyhydroxy substance incompletely esterified with a higher molecular weight fatty acid, and (2) a cation-active substance in the form of a salt of a nitrogenous compound in which an aliphatic hydrocarbon radical containing from 8 to 18 carbon atoms is directly attached to nitrogen.

9. An emulsion containing oleaginous material, aqueous material, and small proportions of (1) glycerol incompletely esterified with a higher molecular weight fatty acid, and (2) a cation-active substance in the form of a quaternary ammonium compound in which an aliphatic hydrocarbon radical containing at least 8 carbon atoms is directly attached to the nitrogen atom.

10. An emulsion containing an oleaginous material, an aqueous material, and small proportions of (1) a cation-active substance in the form of a salt of a nitrogenous compound in which an aliphatic hydrocarbon radical containing from 8 to 18 carbon atoms is directly attached to nitrogen, and (2) a non-ionic substance in the form of a fatty acid derivative of an aliphatic hydroxy compound, the carboxylic acid radical of which contains at least 8 carbon atoms, said derivative containing at least one unesterified hydroxy group in the radical of the aliphatic hydroxy compound.

11. A non-alkaline emulsion containing oleaginous material, aqueous material, and small proportions of (1) a cation-active substance in the form of a salt of a higher molecular weight alkyl non-tertiary amine, and (2) a higher molecular weight fatty acid mono-ester of an aliphatic polyhydroxy substance.

12. An emulsifying agent comprising a mixture of a cation-active substance in the form of a tetra-alkyl ammonium halide and an aliphatic polyhydroxy substance incompletely esterified with a higher molecular weight aliphatic carboxylic acid.

13. An emulsifying agent comprising a mixture of a cation-active substance in the form of a pyridinium halide having directly attached to the nitrogen thereof a hydrocarbon radical containing at least 8 carbon atoms, and a higher molecular weight fatty acid mono-ester of an aliphatic polyhydric alcohol.

14. A cosmetic acid-emulsifying agent comprising a mixture of a cation-active substance in the form of a pyridinium halide having directly attached to the nitrogen thereof a hydrocarbon radical containing at least 8 carbon atoms, and monostearin, the monostearin being present in largely predominating proportions.

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