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O. I. LUNDBERG ET AL

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CLOSED DIE MOLDING A DETERGENT BAR

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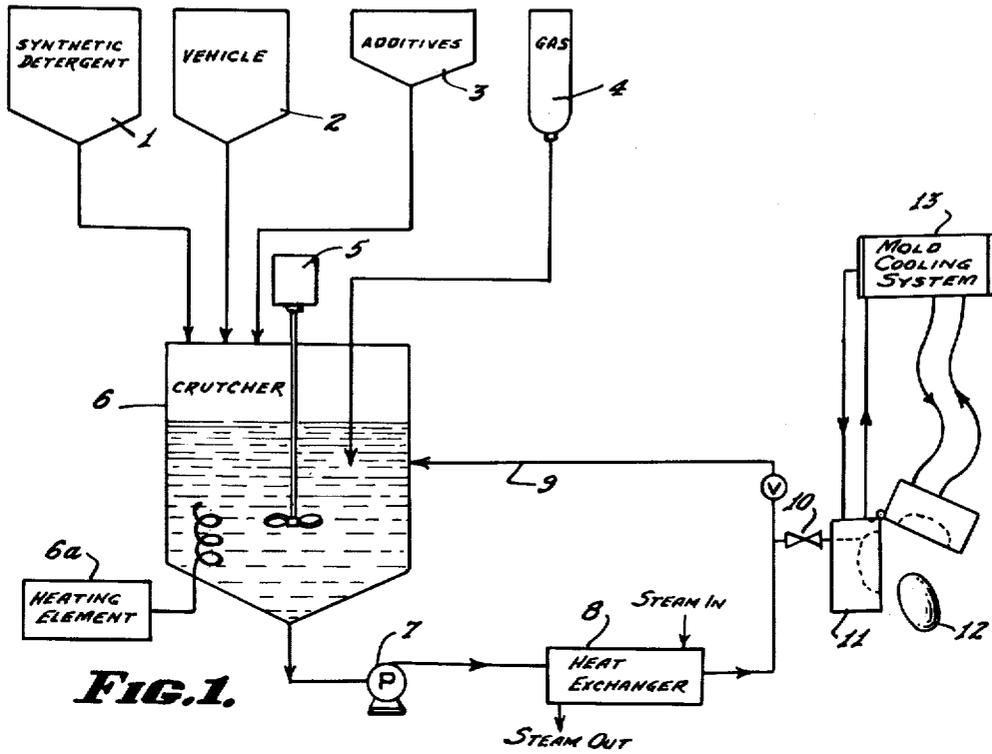


FIG. 1.

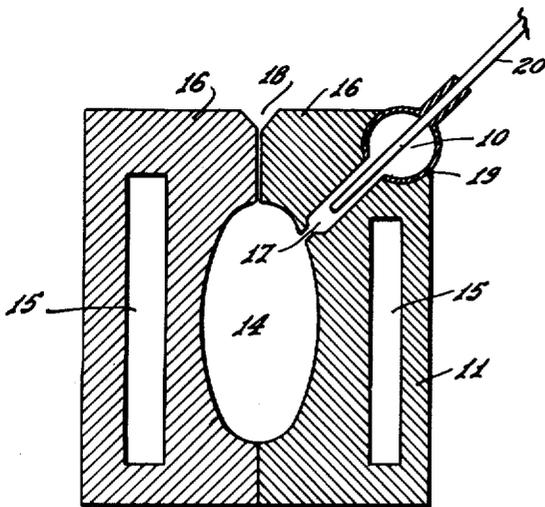


FIG. 2.

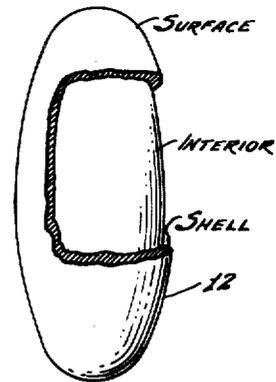


FIG. 3.

INVENTORS.
OLLE I. LUNDBERG AND
JOSEPH BLINKA,

BY *Allen + Allen*

ATTORNEYS.

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CLOSED DIE MOLDING A DETERGENT BAR

Olle I. Lundberg and Joseph Blinka, Springfield Township, Hamilton County, Ohio, assignors to The Procter & Gamble Company, Cincinnati, Ohio, a corporation of Ohio

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This invention relates to a process for closed die molding a substantially non-soap synthetic detergent composition in the form of a toilet bar having outstanding characteristics.

It is an object of this invention to provide a fluid mixture of synthetic detergent and a binder vehicle which can be closed die molded and solidified and which results in a detergent bar having desirable properties of milled toilet bars while being free from undesirable properties of milled toilet bars.

Another object is to provide a closed die molding process for making synthetic detergent bars which utilizes a fluid, detergent-containing mixture capable of rapidly forming a strong shape retaining shell in a substantially closed precooled mold whereby a comparatively short mold dwell time permits rapid production of such bars.

Another object is to provide a process for making a synthetic detergent bar in which air or other gases are dispersed in the fluid detergent composition thereby resulting in a bar which will float in water.

A further object is to provide a process for making synthetic detergent bars free from cleavage planes and orientation of structure.

Another object is to provide means for solidifying a synthetic detergent composition in a phase condition corresponding to that achieved by working or milling.

A still further object is to provide a closed die molding process for making synthetic detergent bars which process overcomes disadvantages inherent in conventional milling processes.

The description of the process employed and the detergent bar produced by the process, which is hereinafter more fully set forth, will be more clearly understood when taken in conjunction with the drawing which shows a flow diagram in FIGURE 1, an example of a suitable mold for the bar in FIGURE 2, and a cut-away view of a finished closed die molded bar in FIGURE 3.

The present invention is based on the discovery that if a detergent composition containing a normally solid synthetic detergent (classified herein as "non-soap") and a proper binder-vehicle can be injected into a substantially closed precooled bar mold, while in a fluid condition (having the proper viscosity characteristics as hereinafter described), the ultimately solidified detergent bar will be in a crystalline phase condition corresponding to that of a bar of the same composition which has been worked in a plastic state, providing the fluid composition is cooled in the mold from a nigre or nigre-plus-crystals phase.

Hitherto in the industry it was understood that bars could be formed either by framing or by a process, such as milling, involving working the composition in a plastic state. Framing methods, in which neat soap or synthetic detergent stock is semi-fluid, produce bars which are generally weaker and softer than milled bars, are limited to a rectangular shape and do not have the smooth shiny surface characteristic of milled bars. Moreover, framed or cast bars are slowly and unevenly cooled and tend to have oriented structure, cleavage planes and segregation of ingredients. Machines and methods for the continuous framing or casting of soap bars have been proposed but have not experienced widespread use apparently because they have not overcome the basic disadvantages of

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framed bars and processes for making them. Framing, to all intents and purposes, is no longer used for the manufacture of toilet bars.

Processes for making toilet detergent bars which involve working the detergent-containing material in the plastic state include the well known milling process on one hand and the "freezer" process described in U.S. Patent 2,295,594 to Mills on the other. But it has always been understood that a process of working a soap composition in a plastic condition was necessary to secure a desirable crystalline condition, a desirable texture, and a desirable solubility in a toilet bar. Bar making procedures involving working in a plastic consistency (which are necessary in the case of a soap composition) have always hitherto been considered by the art to be necessary in the case of a synthetic detergent composition. The synthetic detergent bars which have heretofore met with a significant degree of commercial success are made by conventional soap milling processes using binders and plasticizers which impart sufficient plasticity to the synthetic detergent and result in suitable finished bar characteristics.

Substantially non-soap synthetic detergent bars have long been desirable because of their ability to resist precipitation and the formation of curds by inorganic salts imparting hardness to water. Commonly marketed soap bars are subject to this undesirable precipitation and curd formation.

The synthetic detergents which are normally solid at room temperature and which are useful for bar formulation do not readily bind themselves with water and do not readily soften with heat or moisture sufficiently to enable formation into bars in the manner that soap and water are formed into a workable plastic mass for processing into strong usable bars. Moreover, bars made only of synthetic detergents tend to absorb moisture more rapidly than soap bars, thus shortening their useful life and making them smeary and unattractive in appearance during use. Before synthetic detergents can be used in a practical bar form, they must be combined with a compatible binding agent that gives the bar strength and that reduces the penetration of moisture into the bar. A suitable binding agent should not impart undesirable characteristics to the bar or adversely affect detergency and lathering.

Consequently, while the art has suggested for synthetic detergent compositions bar producing methods which are effective with soap compositions, particularly milling, it has not hitherto been known that any bar product could be made (having the texture and other characteristics of a milled soap or detergent bar) from a composition of synthetic detergent and a binder-vehicle, excepting by a procedure involving working the composition in plastic state.

The discovery that a synthetic detergent bar could be produced having the texture, solubility, and other initial appearance and performance characteristics of a milled product formed of the same material, providing the composition is cooled from or through a nigre or nigre-plus-crystals phase condition, makes possible the attainment not only of those advantages hitherto secured in milled products, but also of other advantages which hitherto could not be secured at all. Also a number of the disadvantages of milled products are avoided.

The desirable properties of milled detergent bars include strength, hardness, firmness, smoothness, shiny surface and rounded shape (from stamping). However, milled bars can be made in only a limited number of shapes because they must be cut and stamped in a relatively firm form. Moreover, milled bars, because the material from which they are made is plodded, extruded

and stamped, have an oriented structure (ordered, aligned, or arranged along the axis of extrusion) and a tendency to have cleavage planes in the bar. Cleavage planes tend to cause weakness within the bar and because of alternate wetting and drying, tend to result in the wet-cracking of the bar along the planes during washstand use. Wet cracks are undesirable because they are conducive to fracturing of the bar, and often the open cracks become filled with dirt, leading to an unsightly bar.

The freezer process, in which floating soap bars can be made, also involves extrusion and the tendency to have oriented structure and cleavage planes in the bar. Floating bars are desirable and many methods have been proposed to make floating milled bars but none has met with any commercial success.

The closed die molding process of the present invention makes it possible to avoid the disadvantages of milled bars, to obtain the advantages of milled bars and to obtain advantages hitherto unobtainable in other bar making processes. Bars of any shape, with or without imprinted wording or designs thereon, can be easily and rapidly made and such bars will be firm and have a smooth shiny surface like milled bars. Bars which will float in water can be formed by injecting an appropriately aerated fluid detergent composition. Multi-colored bars can be made by injection of more than one differently colored detergent mixture. Closed die molding results in the cooling and solidification of a fluid detergent composition in a static state resulting in a bar free from the oriented structure and cleavage planes formed in bar making processes which involve plastic working.

The closed die molding processes of this invention involves the rapid injection through a comparatively small orifice, of a basically non-soap fluid mixture of synthetic detergent and a binder-vehicle, capable of rapid solidification to a shape sustaining form, into a substantially closed precooled mold. After solidification to at least a shape-sustaining form, the bar is ejected from the mold for further cooling as necessary. The resulting bar has outstanding characteristics and does not form hard water curds. Air or other gases can be optionally dispersed intimately in the fluid mixture, especially if a bar capable of floating in water is desired. The dispersed gas forms confined voids on cooling.

The main problems encountered in successfully making detergent bars by closed die molding were the provision of a suitable mixture of synthetic detergent and vehicle and suitable conditions for the process. Such a suitable mixture must be fluid, capable of rapid solidification at temperature within practical ranges and capable of forming a shape sustaining shell without necessarily complete solidification in order to permit commercially feasible production rates. Such fluid mixtures have not been used in the art. Mixtures of synthetic detergent, water and various binders used to make milled bars are heavy plastic masses during milling. Means are not known in the art for making such mixtures fluid enough for closed die molding without damaging them by the use of high temperature, without formulating the mixtures so that a useful detergent toilet bar is not obtained or without introducing difficulties, such as undesirable shrinkage or foaming, into the bar molding process.

The surprising observations that are made are that by proper choice of ingredients, processed as hereinafter described, a bar having outstanding characteristics is obtained without milling or working and that the solidified bar has crystalline characteristics (as determined by X-ray diffraction analysis) which are substantially the same as the crystal characteristics of a bar made of substantially the same ingredients milled or worked in a plastic condition by conventional processes. It is well known that solid hydrated soap can be obtained in at least three different crystalline forms having different

physical and performance characteristics and that the form obtained is dependent on the method by which the soap is processed. For example, framed soap is usually predominantly in the omega phase and can be transformed into the beta phase (having markedly different and superior characteristics) by milling or mechanical working.

In connection with the study of the phase (temperature-composition) behavior of the molten dispersions of synthetic detergent in the fatty vehicle which are closed die molded in accordance with the present invention, it was discovered that the dispersion must be cooled through the nigre (isotropic liquid) plus crystals phase. Preferably it is cooled from this phase condition as well as through it although it can be cooled from the nigre phase and then through the nigre plus crystals phase if excessive temperatures as hereinafter described are avoided. Mixtures of vehicle and synthetic detergents in the neat or middle (anisotropic liquid) phase are not suitable for closed die molding because of the excessive viscosity of those phases and the tendency for undesirable complexes to form in those phases.

It is surprising that successful closed die molding requires cooling the molten dispersion through the nigre plus crystals phase and the avoidance of neat and middle phases since there is nothing in the art of soap bar manufacture which would give such an indication. Neat soap, while more fluid than other soap phases used in soap bar manufacture, is a heavy viscous fluid. Neat soap is used in the framing method for making bars. The "freezer" process utilizes a predominantly neat plus crystals phase which is a heavy plastic mass. The even heavier plastic mass used in making milled soap bars is in a nigre plus crystals phase (with some neat soap), and is unsuitable for use in the framing method. Thus, the closed die molding process of this invention utilizes a detergent-containing mass having a physical condition and phase relationship foreign to conventional soap bar making processes. Closed die molding produces bars having desirable properties characteristic of milled bars but, because the detergent-containing mass is not mechanically worked as is done in milling, the closed die molded bar has additional valuable properties not found in milled bars.

Synthetic detergents

The non-soap synthetic detergents found to be useful in this invention may be broadly designated as the anionic, normally solid, water soluble salts of organic sulfuric reaction products having in their molecular structure an alkyl or acyl radical of carbon atom content within the range of about 10 to about 18 carbon atoms and a sulfonic acid or sulfuric acid ester radical. These salts, more specifically hereinafter defined, were found to possess the properties required for efficient execution of the closed die molding process of this invention and also for obtaining outstanding characteristics in the finished bar. These normally solid salts are readily dispersible in the molten vehicle. They remain uniformly dispersed in the melt upon injection and cooling. They result in firm, strong smooth bars which lather and clean well. In use, the bars do not become unduly slimy, waste away, or crumble and do not form wet cracks which collect dirt.

It was observed that only the normally solid anionic non-soap sulfate and sulfonate detergents herein defined form satisfactory bars. Anionic detergents which are normally liquid or pasty in form result in bars which are undesirably soft, weak and slimy in use.

Important examples of normally solid synthetic detergents which form a part of the outstandingly useful compositions of this invention include sodium and potassium alkyl glyceryl ether sulfonates, especially those ethers of higher fatty alcohols derived by the reduction of coconut oil; the reaction product of higher fatty acids with sodium

or potassium isethionate, where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of a higher fatty acid amide of a methyl taurine in which the higher fatty acyl radicals, for example, are derived from coconut oil; sodium or potassium alkyl benzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms in either a straight chain or preferably a branched chain which is derived from polymers of propylene; dialkyl esters of sodium or potassium salts of sulfosuccinic acid, for example the dihexyl ester; sodium and potassium alkyl sulfonates and sulfates, especially those alkyl sulfates derived by sulfation of higher fatty alcohols produced by reduction of oils of the coconut oil group, such as coconut and palm kernel oils; sodium and potassium salts of sulfated or sulfonated monoglycerides derived, for example, from coconut oil; sodium or potassium salts of the higher fatty alcohol esters or sulfocarboxylic acids, for example, the sodium salt of the lauryl alcohol ester of sulfoacetic acid; and others known in the art a number being specifically set forth in U.S. Patent No. 2,486,921 issued to Byerly on November 1, 1949.

The above list of normally solid non-soap detergents is given only for the purpose of illustrating the types of detergent compounds useful in the practice of this invention and it will be appreciated that the scope of the invention is not thereby limited.

As those versed in the art well know, certain of the normally solid, anionic, non-soap detergents and their homologues have more desirable solubility, latherability, hygroscopicity and mildness characteristics than others and the detergents selected for use can depend on the particular characteristics to be emphasized. The preferred synthetic detergents for the process and product of this invention are the water soluble, alkyl glyceryl ether sulfonates, acyl isethionates and N-methyl N-acyl taurides in which at least 50% of the alkyl and acyl radicals contain 12 carbon atoms in a straight saturated chain.

Vehicle

The binder vehicle material used in the practice of this invention should be one that forms with the synthetic detergent a fluid molten dispersion which upon cooling through the nigre plus crystals phase, forms a bar of outstanding physical and performance characteristics. It was found that to fulfill these requirements the vehicle should have certain properties as hereinafter described.

First, the vehicle should be a normally solid, organic material having a melting point in the range of about 120° F. to about 220° F., preferably about 130° F. to about 190° F. These ranges are above the usual maximum summer temperature that the bar must resist. Vehicles which melt above about 220° F. are undesirable because of high heat requirements in the process. Moreover, the vehicle should have a comparatively sharp melting point and must be capable of changing from a fluid state to a relatively strong crystalline solid within a temperature drop which will be feasible in view of the permissible cooling time within the mold. The vehicle material must have a comparatively sharp melting point within the above melting point range even when it is modified by the dispersion in it of the detergent component or other additives as hereinafter described. Soap, which is used as a binder in some commercial detergent bars, is unsatisfactory as the vehicle in the process of this invention since it is too viscous and melts and solidifies comparatively slowly over a rather broad temperature range; but minor amounts of soap may be beneficial as hereinafter described.

Second, the vehicle, in its normally solid form in the finished bar, should have low solubility in water but have an affinity for water so that the behavior of the solidified dispersion of synthetic detergent and vehicle is comparable, in washstand use, with the conventional fatty acid soap toilet bars such as those made from the sodium

salts of fatty acids derived from a fat and oil mixture containing about 75% tallow and about 25% coconut oil. The vehicle should have some affinity for water in order to obtain desirable lathering characteristics in the bar.

However, if a vehicle material is so soluble in water that it results in a bar which dissolves quickly, wastes away or becomes unduly soft or slimy in washstand use, it is unsuitable for a vehicle. On the other hand, if a material has such a low affinity for water that it results in a bar which does not release the synthetic detergent material during rubbing for detergency in the form of lather, it is unsuitable for a vehicle. Moreover, a material which has too low affinity for water results in a bar with a gritty-draggy feeling to the hands making it undesirable for personal use.

The materials which were found to be useful as the vehicles in the process and products of this invention and which have low solubility in water, an affinity for water, and comparatively sharp melting points within the above-mentioned ranges, include saturated higher molecular weight fatty acids, saturated higher molecular weight fatty alcohols, and mono- and di-esters of glycerol, ethylene glycol or di-ethylene glycol and saturated higher molecular weight fatty acids. Strong, firm, smooth surfaced bars can be produced using these vehicles. It was found that only the saturated fatty acids and their above-mentioned derivatives can be used since they are normally solid; have comparatively sharp melting points above about 120° F. and are substantially resistant to oxidation. Because of the heating in the process, appreciable amounts of unsaturated fatty acids, and their derivatives, being oxidizable, are undesirable although small amounts can be tolerated, especially those with only one double bond. Odors of oxidized fatty acids may interfere with desired perfuming. The fatty vehicles found to be most useful in the practice of this invention are those with carbon atom chains in the fatty radical ranging in length from about 16 to about 22, preferably 16 to 18. However, any of the above mentioned fatty vehicles, or a mixture thereof, with a melting point in the range of about 120° F. to about 220° F. is useful.

Examples of the useful fatty vehicles include palmitic acid, stearic acid, arachidic acid, behenic acid, the mono- and di-esters of glycerol, ethylene glycol or diethylene glycol and such fatty acids, cetyl alcohol, stearyl alcohol, arachidyl alcohol and behenyl alcohol. Minor amounts (not substantially in excess of about 5%) of saturated fatty vehicles with carbon atom chains of 14 or 24 such as myristic acid, lignoceric acid, the mono- and di-esters of glycerol, ethylene glycol or diethylene glycol and such fatty acids, myristyl alcohol and lignoceryl alcohol, can be tolerated in the melt and finished bar and even can be beneficial. Other normally solid materials having a low solubility in water and an affinity for water similar to these fatty vehicles and having a melting point in the range of about 120° F. to about 220° F. can be used. Fatty acids are preferred vehicles.

The fatty materials used for the vehicles of this invention have the ability to permit incorporation of a gas, such as air or nitrogen, intimately dispersed in the melt used in the closed die molding process of this invention. It is desirable to be able to incorporate gas in a material used to make detergent bars because it is an economical method of increasing the volume of the bar, and it can result in a bar of reduced specific gravity capable of floating in water.

Normally solid petroleum derivatives with melting points within the range of about 120° F. to about 220° F. such as paraffin are not satisfactory vehicle materials because they do not have an affinity for water. Petroleum derivatives, even when associated with a large amount of synthetic detergent, severely inhibit the lathering and detergency properties of the bar. They are difficult to disperse in water, often produce a greasy scum

in the water and impart a poor texture to the bar. Very minor amounts could be tolerated, however.

Proportions of vehicle and synthetic detergent

The molten mixtures used in the process of this invention contain by weight an amount of vehicle, an amount of synthetic detergent and, if desired, amounts of vehicle modifiers and/or additives, as hereinafter described. In the following discussion of proportions of vehicle and synthetic detergent, it is to be understood that combinations which do not total 100%, include such modifiers and/or additives to total 100%. Moreover, the proportions of ingredients in the molten mixture are substantially the same as those in the resulting finished bar.

Even though the materials used as vehicles in producing the bars of this invention are only sparingly soluble in water, they readily disperse in water upon rubbing and lathering of the bar because of their favorable affinity for water and their close association in the bar with the synthetic detergent.

Vehicle materials constitute from about 22% to about 50%, preferably about 24% to about 35%, by weight of the molten mixture used in the process of this invention. Up to about 50% the amount of vehicle present in the melt results in a tolerable performance "load" in the finished bar. When up to about 50% vehicle is present in the finished bar, the amount of synthetic detergent used to cause dispersion of the vehicle in water does not unduly affect the lathering and detergency of the bar. However, if the amount of vehicle in the finished bar exceeds about 50%, the excess vehicle acts as a more pronounced performance load in that it unduly inhibits the lathering properties and solubility of the bar.

At least about 22% of the melt used in closed die molding the detergent bars of this invention should constitute vehicle. It has been found that a melt containing less than about 22% vehicle cannot be made sufficiently fluid, at the temperature desired, to be properly utilized in the process of this invention. The properties and requirements of melt fluidity are hereinafter more fully described.

The molten mixtures used in the process of this invention contain from about 35% to about 7%, preferably about 40% to about 60%, by weight of synthetic detergent. Amounts of detergent less than about 35% of the finished bar do not result in a bar with satisfactory lathering or detergency properties. Amounts of synthetic detergent greater than about 70% are unnecessary to produce a toilet bar of outstanding lathering and detergent characteristics.

It has been found that, within these percentage ranges of synthetic detergent and vehicle, greater proportions of synthetic detergent to vehicle result in bars which will lather better than those with greater proportions of vehicle. It has also been found that, within these ranges, greater amounts of vehicle result in more favorable closed die molding characteristics. The preferred ratio range of synthetic detergent to vehicle is about 2.5:1 to about 1.2:1.

The term "normally-solid" when used in connection with the description of this invention means a substantially solid crystalline form at ordinary atmospheric temperatures and pressures, the temperatures being those ranging up to about 110° F.

Formation of molten dispersion

To form the melt used in the molding process of this invention, the synthetic detergent and the vehicle can be melted together and agitated or the detergent can be dispersed with agitation in molten vehicle. The melt is formed in a fluid injectable state. This state requires that the synthetic detergent be substantially uniformly dispersed in the liquid vehicle and that the viscosity of the melt be within a range of from about 2,000 to about

50,000 centipoises at the conditions of injection. Viscosity of the melt is dependent on the intensity of shearing force agitation and on temperature; it is a function of the composition and phase of the melt. Continuous agitation of the melts used in the injection process is essential for maintaining uniform dispersion of the melt components and a viscosity within the aforementioned range.

A viscosity within the above range is obtainable when the temperature and composition of the melt are such that the melt will cool through the nigre plus crystals phase. The melt can be in the nigre plus crystals phase when it is injected or it can be in the nigre phase when it is injected if excessive temperatures as hereinafter described are avoided. If the melt is initially in the nigre phase, it will always cool through the nigre plus crystals phase; however, the melt is preferably initially in the nigre plus crystals phase since lower melt temperatures are preferred as hereinafter described.

The viscosity of the melts can be measured in two ways. A viscometer, such as the Brookfield Viscometer, placed in the melt will give a reading directly in centipoises. The Brookfield Viscometer is a concentric cylinder rotational type of viscometer the principle of which is described in volume 8 of the Journal of the Society of Cosmetic Chemists, pp. 282-300 (1957) along with other types of viscometers which could be used.

Viscosity can also be measured using the Hagen-Poiseuille equation which is based on the measurement of pressure drop of a liquid flowing in a tube. This equation is discussed in "Elements of Chemical Engineering" by Badger and McCabe (1936) on page 33. The equation gives viscosity in English units (pounds per foot second); this can be converted to centipoises since one English unit equals 1.488 centipoises.

The melts used in the process of this invention exhibit a thixotropic behavior which results in a high apparent viscosity at low rates of shear and a decreasing viscosity at increased rates of shear. The viscosity of the melts varies with changes in the types and proportions of detergent and vehicle in the melt and with the phase of the melt.

A melt having a viscosity in the range of about 2,000 to about 50,000 centipoises at injection conditions is thick enough so that it will not undesirably splash in the mold, entrap air or run out of the mold air vents and is thin enough to permit complete filling of the mold prior to solidification of any composition therein which would have to be displaced during a continuation of the filling and thin enough to avoid excessive injection pressures.

Substantially uniform dispersion is necessary to obtain, from the closed die molding processes of this invention, a homogeneous bar which is firm, strong and smooth. Uniform dispersion results in uniform wearing of the bar ingredients when the bar is lathered. The uniform dispersion of the dissimilar ingredients of the bar composition of this invention provides its good physical characteristics. Materials used as the vehicle component are usually brittle alone and the synthetic detergents used are usually noncohesive alone. However, when uniformly combined in the above mentioned ranges, these components result in a strong, firm, smooth bar which will not become unduly slimy in use and which is in a crystalline phase condition corresponding to that found in milled synthetic detergent bars.

As used herein in connection with the molten mixtures of synthetic detergent and vehicle, the terms "dispersion" and "disperse" are intended to include "solution" and "dissolve." The synthetic detergent is at least in part soluble in the molten fatty vehicle. Dissolved detergent will be in the nigre portion, and the undissolved detergent will be in the crystals portion, of the nigre plus crystals phase. However, solubility of the detergent in the molten vehicle varies with the type of detergent and the temperatures of the melt. Solubility increases with higher temperatures toward complete solution in the nigre phase.

Whether the synthetic detergent is uniformly dispersed in the melt in the form of a solution, in the form of crystals or somewhere in between, the processing characteristics are not noticeably affected as long as other processing conditions as described herein are observed.

It has been found that the proper viscosity for a fluid injectable state can be obtained by maintaining the melt at a temperature in the range of about 160° F. to about 300° F. depending on the melting point of the melt. Preferred temperatures are found in the range of about 180° F. to about 250° F. Lower temperatures in these ranges are usually desirable to reduce the heat requirements in the process and to reduce the amount of cooling required to solidify the bar provided the melting point of the melt permits such a temperature lowering. If temperatures higher than about 300° F. are used, there is danger of the ingredients of the melt discoloring, forming odors or decomposing. Moreover, high temperatures also encourage the formation of undesirable complexes and other chemical combinations of the components. Such complexes and combinations tend to make the melt more viscous and result in a soft bar having inferior lathering properties.

The temperature in these ranges at which any given molten dispersion of vehicle and synthetic detergent is in a fluid injectable state depends on the types and proportions of vehicle and detergent involved, eutectic effects which may result from their combination and the melting point of the vehicle and intensity of melt agitation.

Vehicle modifiers

Depending on the melting point of the vehicle, the proper viscosity for a fluid injectable state of the melt can ordinarily be obtained by adjusting the temperature of the melt between about 160° F. and about 300° F., preferably about 180° F. to about 250° F., the melt thinning as the temperature is increased. However, since it is usually desirable to use temperatures in the lower part of these ranges, it has been observed that certain materials when added to the molten dispersion reduce its viscosity, thus permitting lower injection temperatures. From 0% to about 8% of organic vehicle modifiers can be used. Vehicle modifiers can broadly be classed as alkylene glycols having molecular weights up to about 150 and mono- and di-esters of such alkylene glycols and fatty acids containing 5 to 18 carbon atoms, aliphatic monohydric alcohols containing 1 to 3 carbon atoms, esters of phthalic acid and fatty alcohols containing 5 to 18 carbon atoms, and glycerol. Specific examples are propylene glycol, ethylene glycol, diethylene glycol, triethylene glycol, hexylene glycol, glycerol, ethanol, methanol, isopropanol, propylene glycol monocaproate, propylene glycol monolaurate, propylene glycol dilaurate, dicaprylyl phthalate, dilauryl phthalate and the like. Propylene glycol and its lauric acid esters are preferred.

Surface active agents, dialkyl sulfosuccinates, e.g., sodium dioctyl sulfosuccinate, are effective vehicle modifiers when used instead of or in addition to the above modifiers in amounts up to about 8%.

Ordinarily, vehicle modifiers are used in only sufficient amounts to obtain the desired viscosity at a desired temperature, since excess amounts of vehicle modifiers may tend to unduly soften the finished bar.

Closed die molding process

The process used to closed die mold detergent bars from the molten dispersions described above can be more clearly described using the flow diagram contained in FIGURE 1 of the drawings. It will be understood that this description is merely illustrative and the invention is not limited thereto.

The synthetic detergent from its storage 1 and the vehicle from its storage 2 are delivered to the crutcher 6 where these ingredients are substantially uniformly dis-

persed in a fluid injectable state using the agitator 5 and supplying heat to the crutcher, for example, with a steam jacket or steam coils 6a. Vehicle modifiers, perfumes or other additives can be added to the crutcher 6 from their supply 3, before, after or while the vehicle and synthetic detergent are delivered.

If gas is to be incorporated in the melt in the crutcher 6, for example in order to obtain a finished bar 12 which will float in water, the gas is introduced from its source 4. The entire crutcher 6 can be under gas pressure or the gas can be injected into the melt under pressure. Gas such as air which is occluded in dry ingredients tends to remain when the ingredients are melted. Occluded gas plus gas which is entrapped during agitation of the melt in the crutcher can be enough to result in a bar which will float on water. Gas can be removed from the melt by drawing a vacuum on the crutcher 6. This may be done to remove occluded and entrapped air so that a controlled amount of gas such as nitrogen can be later introduced in the melt under pressure. Specific gravities of the finished bar 12 can range from about 0.5 to about 1.1 (substantially gas-free) by controlling the amount of gas in the melt. A specific gravity of about 0.9 is preferred for a bar which floats on water.

When the ingredients of the melt are substantially uniformly dispersed in a fluid injectable state, the melt is circulated through the injection circuit 9, a pipeline which contains a heat exchanger 8 used to stabilize the temperature of the melt and which continuously recirculates the melt through the crutcher 6. This continuous recirculation supplements the action of the agitator 5 in the continuous agitation of the melt which is essential to maintain the proper viscosity and uniform dispersion of the melt as hereinbefore described. If the molten dispersion is not continuously agitated, it would tend to become viscous and set up and the components of the melt would tend to separate. A pump 7 maintains the circulating and injecting pressure. Pressures in the range of from about 1 to about 20 pounds per square inch are satisfactory for injection and pressures in the range of from about 2 to about 10 pounds per square inch are preferred. Pressures which are too high cause splashing in the mold and increase the density of the melt, making a floating bar difficult to obtain.

When forming bars from the molten dispersion circulating in injection circuit 9, the stream is diverted by closing valve 21 and is injected into the mold 11 by simultaneously opening the injection valve 10. Injection valve 10 is shown in more detail as a part of the cross section of the mold in FIGURE 2. The injection valve 10 is closed as soon as the mold 11 is filled and the circulation is resumed by simultaneously opening valve 21. It has been found that molds for conventionally sized toilet bars are filled in from about 0.5 to about 5 seconds, preferably about 1 to 2 seconds. The mold is cooled by cooling system 13.

The construction of a substantially closed mold (or die) suitable for use in the closed die molding process of this invention is illustrated in FIGURE 2 which is an elevation view of the mold and injection valve in cross section. This type of mold is merely illustrative and suitable molds are not limited to the one described. The mold is in two sections. When the molten dispersion is injected into the mold 11 from injection circuit 9 as shown in FIGURE 1, injection valve 10 is opened. The injection valve is opened as shown in FIGURE 2 by moving slidable stopper 20 out from injection port-valve seat 17 through the valve section 19 of the injection circuit. When the injection valve is opened, the molten dispersion is injected into the mold cavity 14 of the bar mold through injection port-valve seat 17. While the mold cavity 14 is being filled, the air contained therein is forced out through vent 18. This vent consists of a slit-like space between the two mold sections and is located at the top of the mold. Vent 18 is closed by

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the melt filling the mold, being chilled and solidified at that point. The mold cavity 14 is closed by returning slidable stopper 20 into the injection port-valve seat 17.

The vent 18 is preferably located near the top of the mold 11 to reduce any tendency of the vent to be sealed by the injected molten dispersion before all air has been displaced from the mold.

The injection port-valve seat 17 can be of a variety of sizes and shapes such as round holes or slits. Round ports about $\frac{1}{4}$ to about $\frac{1}{2}$ inch in diameter result in good injection with a minimum of bar defacement. The size of the injection port can be varied with the injection speed and pressure being used and with the viscosity of the molten dispersion. If the size of the port is increased, more rapid injection at lower pressures are possible. A larger sized injection port may be desirable for use with higher viscosity molten dispersions and injection ports equivalent to 1" or more in diameter may be used.

The shape of mold cavity 14 governs the shape of the finished bar 12 and can be of practically any shape so long as there is no undercutting which would prevent ejection of a whole bar from the mold. The mold 11 is preferably split into halves to facilitate its opening and closing and the ejection of the finished bar 12. It is sufficient if the mold sections meet at the largest perimeter of the bar cavity 14. If the cavity 14 is highly polished, the finished bar 12 has a very smooth shiny surface.

It will be understood that the term "injection" includes any means for introducing the molten stock under pressure into the mold. Suitably arranged movable mold sections and means for introducing the molten stock, such as that shown in copending application Serial No. 830,652, may be used instead of the method herein described.

The mold 11 is precooled so that the injected molten dispersion is solidified to at least a form sustaining shell as rapidly as possible. The mold 11 is enclosed with a hollow core cooling jacket 16. Within the hollow core 15 chilled brine is circulated so that the mold 11 and the mold cavity 14 are cooled. The brine is chilled and circulated in and out of the mold 11 by the refrigerating system 13. Liquids other than brine may be used for the coolant, e.g. fluorinated hydrocarbons such as Freon. The mold 11 can be cooled by other means; for example, the mold 11 can be packed in solid carbon dioxide or the mold 11 could be of finned construction and be cooled by a blast of chilled air.

Process of solidification

When the molten dispersion is injected into the precooled, substantially closed mold, the solidification begins almost immediately in the outermost portion or shell of the molten bar stock and proceeds toward the center of the bar. Injection is very rapid, the mold being filled in about 0.5 to about 5 seconds, preferably about 1 to 2 seconds. Solidification is a function of time and mold temperature. For speed of production, a short period for holding the molten bar stock in the mold is desirable, e.g. less than about 5 minutes, preferably less than about 2 minutes. To obtain such a short period a low mold temperature is desirable. However, extremely low mold temperatures increase refrigeration requirements and may tend to cause the bar to crack because of too rapid cooling. High mold temperatures increase the time that molten stock must be held in the mold for solidification as well as increasing the tendency of the bar to stick to the inner surfaces of the mold. It has been found that the mold should be precooled to a temperature in the range of about -30° F. to about $+40^{\circ}$ F., and preferably to a temperature in the range of about -10° F. to about $+30^{\circ}$ F., for optimum results, such as minimum tendencies for the bar compositions to stick, crack or require long holding times in the mold. The optimum mold temperature within this range varies with the composition of the melt, the melting point of the mix and the temperature of the melt as it is injected into the mold.

Lowering of the melt temperature decreases the thermal cracking tendency at a particular mold temperature.

Ejection of the bar from the mold takes place by opening the mold and removing the bar or allowing it to drop out. Complete solidification is not required before the bar can be ejected from the mold. Moreover, complete solidification within the mold is not desirable, since it unduly slows production. Cooling the molten stock to a point where the bar has a solid shell thick enough and strong enough to allow the bar to retain its shape unsupported, permits ejection of the bar from the mold for subsequent cooling outside the mold and complete solidification even though the interior still may be molten. Further cooling for about 5 to about 10 minutes can be done in a cooled tunnel or room, for example. For toilet bars of the conventional size, i.e. about 75 to 150 cc. (usually about 100 cc.), a solid shell about $\frac{1}{16}$ to about $\frac{1}{8}$ of an inch thick permits ejection from the mold before complete solidification and can be obtained in about 1 to about 2 minutes under the conditions above indicated. The shell, interior and surface of an injection molded bar are shown in FIGURE 3.

The formation of the aforementioned rigid shell is additionally advantageous because it permits the bar to take a surface finish from the mold walls even though the bar is removed from the mold before complete solidification. In a floating bar, the shell has different physical characteristics from the bar interior and results in certain advantages. Study of the bar shell shows that it is about 5% to 10% more dense, and has finer crystalline structure, than the bar interior, apparently because of the more rapid initial chilling of the shell in the mold and the subsequent slower cooling of the bar interior. Since the shell is more dense and has finer crystalline structure than the interior, it acts as a firmer, smoother, less porous coating for the less dense interior. The shell protects the bar interior by reducing water absorption, escape or perfume and marring. Milled and freezer bars, by the nature of their manufacture, do not have such a protective shell.

It has been found that about 3 to about 6 B.t.u.'s of heat must be abstracted by the cooled mold from a body of molten material forming a conventionally sized bar during a commercially feasible time for holding the melt in the mold in order to obtain a strong, form-retaining shell. A total of about 16 to about 25 B.t.u.'s must be abstracted for complete solidification, the remaining heat being abstracted by cooling outside of the mold. This abstracted heat includes heat of crystallization and the sensible heat which is necessary to cool the melt to the crystallization point.

The cooling procedure of the closed die molding process of this invention as applied to the uniform dispersions described herein result in detergent bars of excellent strength smoothness, firmness and uniformity of structure.

In the closed die molding process of this invention the mold is filled rapidly before any substantial solidification, thus avoiding the tendency for orientation of structure and cleavage planes of the detergent bars made by the milling, freezer or framing methods. Therefore, the detergent bars of this invention will not wet-crack because they do not have the orientation of structure and cleavage planes formed in bars made of other processes.

Additives

The normally solid anionic sulfated and sulfonated organic synthetic detergents which are necessary ingredients in the process and compositions of this invention have been previously described. Detergents other than these can be added, if desired, to the molten dispersion in amounts up to about 10%, without substantially detracting from the injectability of the molten dispersion or from the characteristics of the finished bar composition and in many cases may be beneficial. These detergent

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additives can include anionic non-soap synthetic detergents such as higher acyl sarcosinates, (e.g. sodium lauroyl sarcosinate), and nonionic non-soap synthetic detergents such as a high molecular weight (e.g. 8000) condensate of ethylene oxide with a polypropylene glycol (e.g. Pluronic F68) and other nonionic detergents known in the art.

Water-soluble, normally solid, higher fatty acid soaps can be included in the bar composition in amounts up to about 15%, preferably no more than 10%, to give the user of the finished bar an impression of "soap-feel" to which he may be accustomed, although this is entirely unnecessary to realize the advantages of a synthetic detergent bar. Soaps are useful in some combinations of synthetic detergent and vehicle to reduce the tendency of the injected bar to crack on cooling. The soaps which can be used include, for example, the sodium salts of the fatty acids of natural oils and fats such as tallow and coconut oil. Soap in the melt in amounts in excess of about 15% interferes with viscosity control and proper solidification of the molded bar.

For convenience or economic reasons, it may be desirable to "fill" or dilute the bar composition with a normally solid impalpable substance which does not adversely affect the viscosity characteristics of the molten dispersion of synthetic detergent and vehicle, the injection process or the characteristics of the detergent bar composition. Fillers can be used in the bar compositions in amounts up to about 30%, preferably not more than 20%.

Materials which can be used as fillers or diluents for detergent bars are, for the most part, commonly used and well known in the art. These materials are naturally impalpable such as those of a waxy nature or are finely ground to a size of about 75 microns or smaller. Conventional filler materials include: substantially insoluble, finely ground minerals such as talc, feldspar, quartz, calcium carbonate, bentonite, fuller's earth, clay, kaolin; finely ground inorganic salts of low to moderate solubility such as alkali metal, e.g. sodium, phosphates, chlorides and sulfates; finely ground organic materials of low solubility such as starch, calcium and magnesium soaps and polyethylene glycols with molecular weights of 4000 to 20,000. Alkali metal, e.g. sodium, chlorides and sulfates in a fine form usually accompany anionic synthetic detergents as by-products from their manufacture and the incorporation of such salts in the bars of this invention is usually unavoidable. These salts are inert with respect to the product and process of this invention, particularly as shown in Examples 18, 19, 22, 23 and 24. Oxidized starch, sodium sulfate, and polyethylene glycols with molecular weights of 4000 to 20,000 are the preferred fillers.

Many other materials useful in the production of detergent bars can be added to the molten dispersion without substantially affecting the molding process. These materials include minor amounts of perfumes, whiteners such as titanium dioxide, bacteriostatic agents, emollients, dyes and foaming or lathering agents.

Additives can comprise up to about 43%, preferably not more than 35%, by weight of the finished detergent bar. Dispersed additives which are normally solid appear to increase the viscosity of the melt only slightly. Additives which are not normally solid (including vehicle modifiers and water) should not comprise more than about 10% by weight of the finished bar in order to avoid softening of the bar.

Water

The synthetic detergent bar compositions of this invention can be substantially anhydrous. This characteristic is advantageous in that there is no "drying-out" of the bar in storage or use. Drying out is common in milled and "freezer" bars and promotes warping and wet cracking. 5%-15% moisture content is usually a requirement for detergent compositions undergoing milling operations and

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greater amounts are required for "freezer" operations. The ingredients of the bar compositions of this invention can be processed dry, but ordinarily contain up to about 1% moisture. Up to about 5% water can be tolerated in the molten dispersion to be injected. Amounts of water greater than about 5% tend to increase the viscosity of the melt, cause undesirable steam and foaming in the melt, and soften the finished bar.

EXAMPLES

The following examples are given to illustrate the manner in which this invention can be practiced. Its scope is not limited by the ingredients named in the examples since it is apparent that some can be interchanged with each other or equivalents substituted. Likewise, its scope is not limited to the proportions shown in the examples since the proportions can be varied to adjust for variations in properties of substituted equivalent ingredients. All parts are by weight.

Example I.—The following ingredients were added to a crutcher, heated to about 180° F. and agitated for about 20 minutes until the synthetic detergent was dispersed in the fatty alcohol vehicle:

- 55 parts sodium alkyl glyceryl ether sulfonate, the alkyl radical being produced from a fractionated fatty alcohol mixture derived from the reduction of coconut oil and consisting of about 2% decyl alcohol, 66% lauryl alcohol, 23% myristyl alcohol and 9% cetyl alcohol.
- 37 parts stearyl alcohol.
- 5 parts of a mixture of sodium chloride and sodium sulfate as by-products of the detergent salt manufacture.
- 2 parts propylene glycol.
- 1 part perfume.

Nitrogen gas was dispersed and emulsified in the melt by introducing it at about 10 pounds per square inch pressure. The melt was run into the injection system and circulated by pump at about 5 pounds per square inch pressure. A portion of the melt was rapidly injected into the mold which was cooled with refrigerated brine to about 0° F. The dispersion was held in the mold for about 2.5 minutes after which the bar had a strong solid shell about 1/8" thick. The bar was then ejected from the mold even though its interior was still warm and soft. After further cooling the bar was observed to be firm, strong and smooth surfaced. It lathered well in hard or soft water. In washstand use the bar cleansed well and formed none of the hardwater curd and scum common to soap. Upon continued use, no wet-cracking tendency characteristic of milled, framed or "freezer" detergent bars was observed.

The melt was kept continuously circulating and as soon as a finished cooled bar was ejected from the mold, the mold was closed and another portion of the melt was injected into the mold in a manner similar to the first injection with substantially equal results. This process was repeated until the volume of the melt became too small to circulate. A battery of molds can be filled by injection simultaneously to increase the number of detergent bars produced in a given time.

Example II.—The following ingredients were added to a crutcher, heated to about 190° F. and agitated for about 20 minutes:

- 45 parts sodium alkyl glyceryl ether sulfonate described in Example I.
- 3 parts sodium alkyl benzene sulfonate, the alkyl group being derived from polypropylene and averaging about 12 carbons.
- 7 parts sodium N-methyl-N-coconut oil fatty acid taurate.
- 25 parts hydrogenated tallow fatty acid containing about

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- 65% stearic acid, 33% palmitic acid and 2% myristic acid.
 2 parts propylene glycol.
 9 parts oxidized corn starch.
 1 part water.
 1 part perfume.
 7 parts a mixture of sodium sulfate, sodium chloride which accompany the detergent salts as by-products of manufacture.

The molten dispersion resulting was run into the injection system and circulated by pump at about 8 pounds per square inch pressure. Occluded and entrapped air was emulsified and dispersed in the melt. A portion of the melt was rapidly injected into a mold, which was cooled with refrigerated brine to about 5° F. The dispersion was held in the mold for about 3 minutes and the bar was ejected. After further cooling, the bar was firm, strong and smooth surfaced. It floated in water, lathered and cleansed well, was mild to the skin, formed no wash-stand curd and was non-cracking.

Example III.—A detergent bar was closed die molded using the following materials in accordance with the procedure described in Example II except for the changes in conditions listed below:

- 40 parts sodium N-methyl-N-coconut oil fatty acid taurate.
 23 parts hydrogenated tallow fatty acid described in Example II.
 10 parts oxidized cornstarch.
 7 parts propylene glycol.
 1 part water.
 1 part perfume.
 18 parts sodium chloride as a by-product of manufacture of the detergent salt.

The mold was cooled to about 30° F.; the injection temperature was about 180° F.; the injection pressure was about 5 pounds per square inch; the injection time was approximately one second; nitrogen gas was incorporated in the melt; the molten stock was held in the mold for about one minute and the bar with a solidified shell was then ejected. After further cooling the resulting bar was an excellent, floating, strong, non-cracking, mild, rich lathering, toilet bar.

Methanol, ethanol and ethylene glycol can be substituted for the propylene glycol in Example III with substantially equal results both in injection molding and bar performance.

Example IV.—A bar with properties similar to those described in Example II and closed die molded in accordance with the procedure described in that example (except for the changes in conditions listed below) was made of the following ingredients:

- 45 parts sodium alkyl glyceryl ether sulfonate described in Example I.
 30 parts hydrogenated tallow fatty acids described in Example II.
 2 parts propylene glycol.
 1 part perfume.
 7.3 parts oxidized cornstarch.
 4.7 parts of a mixture of sodium sulfate and sodium chloride (by-product of detergent production).
 4 parts sodium alkyl benzene sulfonate described in Example II.
 6 parts sodium salt of sulfated coconut oil fatty alcohol containing about 66% lauryl alcohol, 23% myristyl alcohol, 9% cetyl alcohol and 2% decyl alcohol.

An injection temperature of about 180° F., an injection pressure of about 8 pounds per square inch, a mold tem-

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perature of about -8° F. and a cooling time of about 2 minutes were used.

- Example V.*—A bar with properties similar to those described in Example II and closed die molded in accordance with the procedure described in that example (except for the changes in conditions listed below) was made of the following ingredients:

- 30 parts sodium-N-methyl-N-coconut fatty acid taurate.
 10 parts coconut oil fatty acid ester of sodium isethionate.
 25 parts hydrogenated tallow fatty acid described in Example II.
 7 parts propylene glycol.
 1 part perfume.
 15 17 parts sodium chloride as a by-product of manufacture of the detergent salts.
 10 parts oxidized cornstarch.

- 20 An injection temperature of about 230° F. and an injection time of about 0.5 seconds, a mold temperature of about 30° F. and a cooling time of about 3 minutes were used.

- Example VI.*—The following ingredients were added to a crutcher, heated to about 220° F. and agitated until they were dispersed in the fatty acid vehicle:

- 42 parts coconut oil fatty acid ester of sodium isethionate.
 12 parts stearic acid.
 12 parts palmitic acid.
 5 parts sodium salt of sulfated coconut oil fatty alcohol.
 4 parts dioctyl ester of sodium sulfosuccinate.
 5 parts sodium coconut oil alcohol sulfoacetate.
 35 7 parts sodium coconut oil soap.
 4 parts propylene glycol.
 0.4 part titanium dioxide.
 0.8 part perfume.
 6.8 parts of a mixture of sodium chloride and sodium sulfate as a by-product of manufacture of the detergent salts.
 40 1 part moisture.

- 45 After the resulting molten dispersion was deaerated by drawing a vacuum on the system, nitrogen gas was dispersed therein. The melt was then run into the injection circuit and circulated by pump at about 5 pounds per square inch pressure. A portion of the melt was rapidly injected into the mold which was cooled with refrigerated brine to about 20° F. The dispersion was held in the mold for about one minute which was long enough for a strong, solid, shape-sustaining shell to form. The bar was ejected from the mold and further cooled for about 7 minutes in a cooling tunnel without deformation. Sufficient nitrogen gas had been introduced in the molten dispersion so that the resulting bar had an overall density of about 0.9 and floated in water. The bar was firm, strong and smooth surfaced; it lathered excellently. It exhibited no wet cracking tendencies. When the bar was cut in half, a shell about 1/8 inch thick having a density of about 0.97 was observed.

- 65 In Example VI, propylene glycol monolaurate, propylene glycol dilaurate, propylene glycol dioleate, ethylene glycol monolaurate, ethylene glycol dimyristate, triethylene glycol, hexylene glycol, glycerol and dilauryl phthalate can be substituted for the propylene glycol with substantially equal results in both closed die molding and the performance of the finished bar.

- 70 The following table of bar composition examples will serve to illustrate wide variety of formulations which can be closed die molded according to the process of this invention. All parts are by weight. The formulations include about 1% moisture.

Example.....	7	8	9	10	11	12	13	14	15	16	17	18
Detergent:												
Sodium alkylbenzene (described in Example II)												
Sodium alkyl glyceryl ether sulfonate (described in Example I)	55	55	55	55	55	55	55	51.9	51.9	51.9	55	32.9
Coconut oil fatty acid ester of sodium isethionate												11.3
Sodium salt of sulfated coconut oil fatty alcohol												
Diocetyl ester of sodium sulfosuccinate												
Sodium salt of sulfated coconut oil monoglyceride												
Potassium alkyl sulfonate derived from a mixture of straight chain α olefins												
Vehicle:												
Myristic Acid	0.6					0.2	0.4				1.9	1
Palmitic Acid	9.9			30		3.3	6.6				8.6	16.5
Stearic Acid	19.5		4.5		30	6.5	13.0				8.1	32.5
Arachidic Acid											7.6	
Behenic Acid			25.5								4.8	
Myristyl Alcohol									0.7			
Cetyl Alcohol		30							11.4			
Stearyl Alcohol						20	10		22.4		3.8	
Arachidyl Alcohol											17.6	
Behenyl Alcohol											13.1	
Glycerol Monostearate								34.5				
Diethylene Glycol Distearate												
Ethylene Glycol Monostearate												
Glycerol Dipalmitate												
Additives:												
Propylene Glycol	2	2	2	2	2	2	2	2	2	2	2	
Perfume	1	1	1	1	1	1	1	1	1	1	1	
Polyethylene glycol (mol. wt. 20,000)												
Polyethylene glycol (mol. wt. 4,000)												
Oxidized corn starch	7.2	7.2	7.2	7.2	7.2	7.2	7.2					
Mixture of sodium chloride and sulfate	4.8	4.8	4.8	4.8	4.8	4.8	4.8	10.6	10.6	10.6	11	5.8
Coconut oil soap												

Example.....	19	20	21	22	23	24	25	26	27	28	29
Detergent:											
Sodium alkylbenzene (described in Example II)					5	5	45				
Sodium alkyl glyceryl ether sulfonate (described in Example I)	43.7	29.8									
Coconut oil fatty acid ester of sodium isethionate	15	10.2			55.3	55.3		48.5	48.5	48.5	
Sodium salt of sulfated coconut oil fatty alcohol				4				4	4	4	4
Diocetyl ester of sodium sulfosuccinate				48.2	8.1						
Sodium salt of sulfated coconut oil monoglyceride											
Potassium alkyl sulfonate derived from a mixture of straight chain α olefins											52
Vehicle:											
Myristic Acid	0.7	0.9									
Palmitic Acid	11	14.9				3			9		14
Stearic Acid	21.6	29.5				3			9		14
Arachidic Acid											
Behenic Acid											
Myristyl Alcohol				0.7	0.8						
Cetyl Alcohol				12	13.5						
Stearyl Alcohol				23.3	26.7						
Arachidyl Alcohol											
Behenyl Alcohol											
Glycerol Monostearate						30	24				
Diethylene Glycol Distearate											
Ethylene Glycol Monostearate								28	10		
Glycerol Dipalmitate										28	
Additives:											
Propylene Glycol								40			
Perfume								7	4	4	4
Polyethylene glycol (mol. wt. 20,000)											
Polyethylene glycol (mol. wt. 4,000)			9.3	5							
Oxidized corn starch											
Mixture of sodium chloride and sulfate	8	5.4	6.8	3.4	9.7	9.7	8	8.5	8.5	8.5	5
Coconut oil soap								7	7	7	7

The detergent bars of the examples of this table were firm, strong and smooth, had protective shells and lathered and cleaned well. None exhibited cleavage planes or wet cracking tendencies.

The detergent bars of this invention have outstanding utility as toilet bars, e.g. personal washstand and bath use. However, they are also useful as shaving soaps or for the hand washing of wool and fine fabrics, for example.

Various modifications and variations of this invention will be obvious to persons skilled in the art and it is to be understood that such modifications and variations are to be included within the purview of this application and the spirit and scope of the claims.

What is claimed is:

1. In the process of closed die molding a detergent bar, the steps of (1) forming, for injection, a fluid melt comprising a mixture of from about 35% to about 70% normally-solid, water-soluble, anionic, non-soap, synthetic detergent and from about 22% to about 50% normally-solid fatty vehicle having a melting point between about

120° F. and 220° F. selected from the group consisting of saturated higher molecular weight fatty acids and alcohols and mono- and di-esters of said fatty acids and a polyhydric alcohol selected from the group consisting of glycerol, ethylene glycol and diethylene glycol, by heating said mixture to a temperature in the range of from about 160° F. to about 300° F. and with agitation substantially uniformly dispersing said detergent in said vehicle, the temperature and proportions of said detergent and vehicle being such that the resulting molten dispersion has a viscosity in the range of from about 2000 to about 50,000 centipoises at the conditions of injection and such that said dispersion will cool through the nigre plus crystals phase, (2) continuously agitating said dispersion prior to injection, (3) injecting said dispersion into a substantially closed bar mold, filling said mold, said mold being pre-cooled to a temperature in the range of about -30° F. to about +40° F. and sufficient to form rapidly at least a solid, shape-sustaining shell for said bar, (4) ejecting said bar from said mold.

2. The process of claim 1 with the additional steps of incorporating gas in the fluid melt sufficient to obtain a detergent bar capable of floating in water and subjecting the ejected bar to further cooling for complete solidification.

3. The process of claim 2 wherein the carbon chains in said vehicle range in length from about 16 to about 22, the ratio of synthetic detergent to vehicle is in the range of about 2.5:1 to about 1.2:1, the mixture of synthetic detergent and vehicle is heated to a temperature in the range of about 180° F. to about 250° F. and the substantially closed mold is precooled to a temperature in the range of from about -10° F. to about +30° F.

4. The process of claim 3 in which up to about 8% of a vehicle modifier selected from the group consisting of alkylene glycols having molecular weights up to about 150, esters of said alkylene glycols and fatty acids containing 5 to 18 carbon atoms, aliphatic monohydric alcohols containing 1 to 3 carbon atoms, glycerol, and esters of phthalic acid and fatty alcohols containing 5 to 18 carbon atoms, is added to the molten dispersion in step (1) to reduce viscosity.

5. The process of claim 3 in which the detergent is selected from the group of alkyl glyceryl ether sulfonates, acyl isethionates and N-methyl acyl taurides in which at least 50% of the alkyl and acyl groups respectively contain 12 carbon atoms in a straight saturated chain and the vehicle consists of fatty acids ranging in chain length from 16 to 18 carbon atoms.

6. In the process of closed die molding a detergent bar, the steps of (1) forming, for injection a fluid melt comprising a mixture of from about 40% to about 60% normally-solid, water-soluble, anionic, non-soap, synthetic detergent and from about 24% to about 35% normally-solid fatty vehicle having a melting point between about 130° F. and about 190° F. selected from the group consisting of saturated higher molecular weight fatty acids and alcohols and mono- and di-esters of said fatty acids and a polyhydric alcohol selected from the group consisting of glycerol, ethylene glycol and diethylene glycol, the carbon chains in said vehicle ranging from about 16 to about 22, by heating said mixture to a temperature in the range of from about 180° F. to about 250° F. and with agitation substantially uniformly dispersing said detergent in said vehicle, the temperature and proportions of said detergent and vehicle being such that the resulting molten dispersion has a viscosity in the range of from about 2000 to about 50,000 centipoises at the conditions of injection and such that said dispersion will cool through the nigre plus crystals phase, (2) continuously agitating said dispersion prior to injection, (3) injecting said dispersion into a substantially closed bar mold, filling said mold, said mold being precooled to a temperature in the range of about -10° F. to about +30° F. and sufficient to form rapidly a solid, shape-sustaining shell for said bar, (4) ejecting said bar from said mold, (5) subjecting said bar to further cooling for complete solidification.

7. The process of claim 6 with the additional step of incorporating gas in the fluid melt sufficient to obtain a detergent bar capable of floating in water.

8. The process of claim 7 in which up to about 8% of a vehicle modifier selected from the group consisting of alkylene glycols having molecular weights up to about 150, esters of said alkylene glycols and fatty acids containing 5 to 18 carbon atoms, aliphatic monohydric alcohols containing 1 to 3 carbon atoms, glycerol, and esters of phthalic acid and fatty alcohols containing 5 to 18 carbon atoms, is added to the molten dispersion in step (1) to reduce viscosity.

9. The process of claim 7 in which the detergent is selected from the group consisting of alkyl glyceryl ether sulfonates, acyl isethionates and N-methyl acyl taurides in which at least 50% of the alkyl and acyl radicals respectively contain 12 carbon atoms in a straight saturated chain and the vehicle consists of fatty acids ranging in chain length from 16 to 18 carbon atoms.

10. In the process of closed die molding a detergent bar, the steps of (1) forming, for injection, a fluid melt consisting essentially of a mixture of from about 40% to about 60% normally-solid, water-soluble, anionic, non-soap, synthetic detergent from about 24% to about 35% normally solid fatty vehicle having a melting point between about 130° F. and 190° F. selected from the group consisting of saturated higher molecular weight fatty acids and alcohols and mono- and di-esters of said fatty acids and a polyhydric alcohol selected from the group consisting of glycerol, ethylene glycol and diethylene glycol, the carbon chains in said vehicle ranging from about 16 to about 22 carbon atoms, 0% to about 10% soap, 0% to about 30% normally solid impalpable filler material, and 0% to about 8% propylene glycol to reduce the viscosity of the melt, by heating said mixture to a temperature in the range of from about 180° F. to about 250° F. and with agitation substantially uniformly dispersing in said vehicle said detergent, soap, filler and propylene glycol, the temperature and proportions of said ingredients being such that the resulting molten dispersion has a viscosity in the range of from about 2000 to about 50,000 centipoises at the conditions of injection and such that said dispersion will cool through the nigre plus crystals phase, (2) continuously agitating and circulating said dispersion prior to injection, (3) injecting said dispersion into a substantially closed bar mold, filling said mold, said mold being precooled to a temperature in the range of about -10° F. to about +30° F. and sufficient to form rapidly a solid, shape sustaining shell for said bar, (4) ejecting said bar from said mold, (5) subjecting said bar to further cooling for complete solidification.

11. The process of claim 10 with the additional step of incorporating gas in the fluid melt sufficient to obtain a detergent bar capable of floating in water.

12. The process of claim 11 in which the detergent is selected from the group consisting of alkyl glyceryl ether sulfonates, acyl isethionates and N-methyl acyl taurides in which at least 50% of the alkyl and acyl radicals respectively contain 12 carbon atoms in a straight saturated chain and the vehicle consists of fatty acids ranging in chain length from about 16 to 18 carbon atoms.

13. In the process of closed die molding a floating detergent bar, the steps of (1) forming, for injection, a fluid melt consisting essentially of a substantially anhydrous mixture of from about 40% to about 60% of a detergent selected from the group consisting of alkyl glyceryl ether sulfonates, acyl isethionate and N-methyl acyl taurides in which at least 50% of the alkyl and acyl radicals respectively contain 12 carbon atoms in a straight saturated chain, from about 24% to about 35% of saturated fatty acids ranging in chain length from about 16 to 18 carbon atoms, 0% to about 10% soap, 0% to about 30% normally solid impalpable filler material and 0% to about 8% of a lauric acid ester of propylene glycol to reduce the viscosity of the melt, by heating said mixture to a temperature in the range of from about 180° F. to about 250° F. and with agitation substantially uniformly dispersing in said vehicle said detergent, soap, filler and ester, the temperature and proportions of said ingredients being such that the resulting molten dispersion has a viscosity in the range of from about 2000 to about 50,000 centipoises at the conditions of injection and such that said dispersion will cool through the nigre plus crystals phase, (2) incorporating gas in the fluid melt sufficient to obtain a detergent bar capable of floating in water, (3) continuously agitating and circulating said dispersion prior to injection, (4) injecting said dispersion into a substantially closed bar mold, filling said mold, said mold being precooled to a temperature in the range of about -10° F. to about +30° F. and sufficient to form rapidly a solid, shape sustaining shell for said bar, (5) ejecting said bar from said mold,

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(6) subjecting said bar to further cooling for complete solidification.

14. A closed-die molded detergent bar having a protective shell which is denser than the interior of the bar, said bar being free from the cleavage planes and orientation of structure characteristic of milled detergent bars and said bar comprising from about 35% to about 70% normally solid, water soluble, anionic, non-soap synthetic detergent substantially uniformly dispersed in from about 22% to about 50% normally-solid fatty vehicle having a melting point between about 120° F. and 220° F. selected from the group consisting of saturated higher molecular weight fatty acids and alcohols and mono- and di-esters of said fatty acids and a polyhydric alcohol selected from the group consisting of glycerol, ethylene glycol and diethylene glycol, said bar having sufficient gas dispersed therein so as to be capable of floating in water.

15. A closed die molded detergent bar having a protective shell which is denser than the interior of the bar, said bar being free from cleavage planes and orientation of structure characteristic of milled detergent bars and said bar comprising from about 40% to about 60% normally solid, water soluble, anionic, non-soap synthetic detergent substantially uniformly dispersed in from about 24% to about 35% normally solid fatty vehicle having a melting point between about 130° F. and about 190° F. selected from the group consisting of satu-

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rated higher molecular weight fatty acids and alcohols and mono- and di-esters of said fatty acids and a polyhydric alcohol selected from the group consisting of glycerol, ethylene glycol and diethylene glycol, the carbon chains in said vehicle ranging from about 16 to about 22 in length, said bar having sufficient gas dispersed therein so as to be capable of floating in water.

16. The detergent bar of claim 15 wherein the said detergent is selected from the group consisting of alkyl glyceryl ether sulfonates, acyl isethionates and N-methyl acyl taurides in which at least 50% of the alkyl and acyl radicals respectively contain 12 carbon atoms in a straight saturated chain and the vehicle consists of fatty acids ranging in chain length from 16 to 18 carbon atoms, said bar containing additionally 0% to about 10% soap and 0% to about 30% normally solid impalpable filler material.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,987,484

June 6, 1961

Olle I. Lundberg et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 44, for "7%" read -- 70% --; column 12, line 64, for "of" read -- by --; column 19, line 64, for "carton" read -- carbon --.

Signed and sealed this 21st day of November 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents

USCOMM-DC