

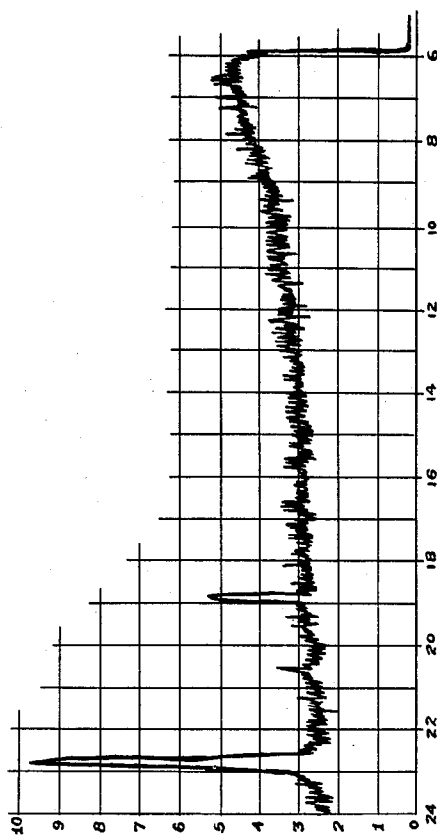
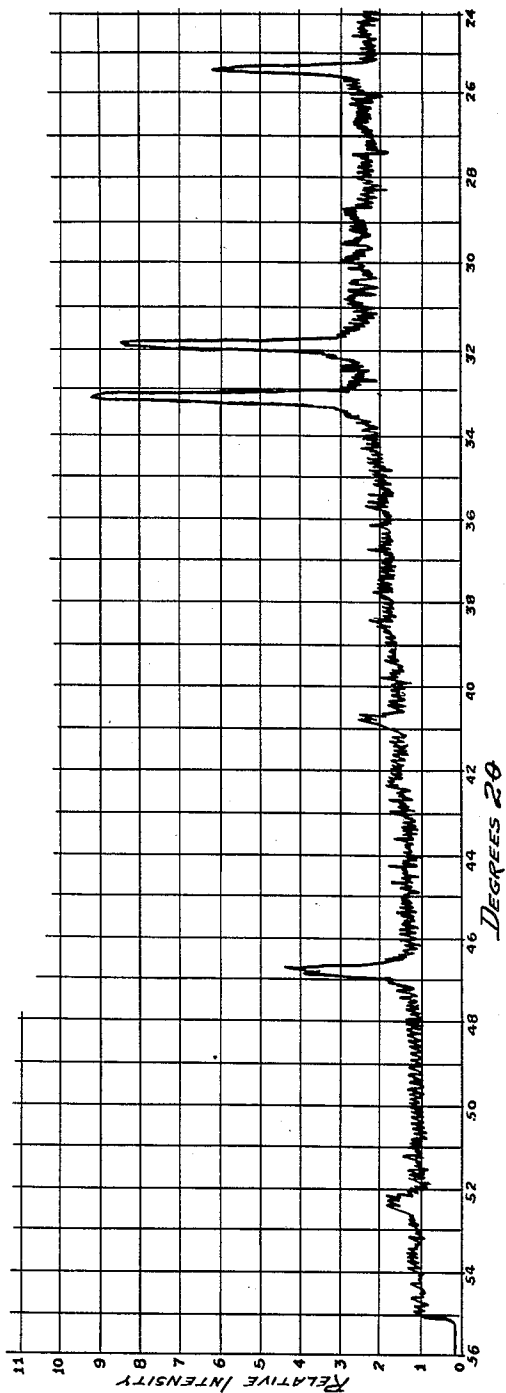
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DETERGENT COMPOSITIONS

Filed Oct. 15, 1956



(CONTINUED)

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2,941,948

DETERGENT COMPOSITIONS

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The present invention relates to mechanically worked compositions consisting largely or entirely of inorganic salts and organic synthetic sulfate and sulfonate detergents and to a method for making such compositions.

Uniformity of composition and of texture, good physical toughness and cohesiveness, and desirable surface appearance and feel are best attained in solid soaps and synthetic detergents by the mechanical working of compositions which have a substantial degree of plasticity. Such worked products are commonly referred to as "milled," even though some alternative means of working such as plodding and/or extruding may be employed in their manufacture.

Sodium soaps and some of the organic sulfate and sulfonate detergent salts have a high degree of plasticity when within suitable ranges of temperature and moisture content, as is well known, and therefore lend themselves admirably to the manufacture of milled soaps and other milled detergents. Inorganic salts, as a rule, are devoid of plasticity and can be incorporated only to a limited extent in milled soaps and milled detergent compositions. When a milled detergent is to be made from a synthetic detergent which is itself low in plasticity, or substantially devoid of plasticity, the amount of ordinary inorganic salt which can be tolerated is quite low. If, in any given case, the amount of unplasticizable inorganic salt is excessive, the composition will lack cohesiveness and toughness, will tend to crumble, will be dull in surface appearance, and undesirable in texture.

Mechanical working is the most practical means by which synthetic detergents containing large amounts of inorganic salts can be made into flake or bar form. Such compositions because of their lack of plasticity are, however, extremely difficult to mill or extrude. They are quite temperature sensitive, abrade the equipment, discolor, and tend to pile up and halt the operation of the mills and extruders. Furthermore, anionic detergents tend to be crystalline and do not readily emmesh water, as do soaps. Some anionic detergents exhibit plasticity within a narrow temperature range. However, even when these detergents are plastic, their plasticity is inadequate to permit good mechanical working in the presence of large amounts of inorganic salts. Without the addition of a plasticizer, or binder such as insoluble soaps, starch, waxes and carboxymethylcellulose, detergent bars or flakes containing large amounts of inorganic salts cannot be made successfully by milling or extruding.

Our discovery of a plastic inorganic salt combination greatly increases the range of formulations of satisfactory milled synthetic detergents. It is particularly advantageous in that it includes tripolyphosphates which are recognized as excellent detergency builders for synthetic detergents. Detergent-tripolyphosphate compositions are comparable to soaps in detergency in soft water and are greatly superior to soaps in detergency in hard water. The second component of our unique plastic inorganic salt complex is sodium sulfate, a material which accom-

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Without the formation of the tripolyphosphate-sodium sulfate complex, which is inherent in the practice of our invention, it would in many cases be necessary to go to the added expense of removing the sodium sulfate before attempting to use the synthetic detergent in making a milled product.

It is an object of this invention to provide mechanically worked organic synthetic detergent compositions containing large amounts of inorganic salts, and to provide a method for making such detergent compositions. It is a further object to provide mechanically worked synthetic organic detergent bars, ribbons and flakes containing, as builders, crystalline inorganic complexes. It is a further object to provide mechanically worked synthetic organic detergent bars, ribbons, and flakes containing, as a builder, a crystalline sodium sulfate-sodium tripolyphosphate complex which can be identified by its characteristic X-ray diffraction pattern. It is a further object to provide heavily built milled detergent flakes which will not crack during processing. Other objects and advantageous features will become apparent from the following detailed discussion.

This invention is based on the discovery of heretofore unrecognized crystalline plasticizable inorganic complexes and, in particular, a crystalline sodium sulfate-sodium tripolyphosphate complex which under certain conditions becomes plastic in nature. The plasticity of these complexes makes possible the production of mechanically worked water soluble, anionic, synthetic organic, detergent compositions containing large amounts of inorganic builder.

One means of accomplishing the mechanical working of the detergent compositions of the present invention is the process of milling. In the milling operation, the plastic detergent composition is passed between a series of rotating rolls, successive members of the series rotating at higher speeds and at lower clearances, the detergent composition being thus subjected to mechanical working, shearing and compacting. The action of the milling rolls can be supplemented by plodding and extruding, whereby the detergent composition is mechanically worked, with shearing and compacting, by being forced through one or more orifices of restricted size by the pressure of an Archimedean screw revolving within a closed barrel. In fact, oft repeated high pressure extrusions through small orifices accomplish a mechanical working and compacting to coherent solid form similar in nature and effect to passage through a series of milling rolls, due to linear flow of the detergent composition under pressure, presumably with adjacent layers flowing at different relative speeds. The mechanical working accomplished by either plodding and extruding or milling results in a rise in temperature, which may be regulated by adding or extracting heat, as desired. It will be understood that our process is capable of producing mechanically worked detergent compositions by passage over and between milling rolls, or by repeated extrusion through restricted orifices, or by an equivalent manner of working or kneading, such as by means of pin-barrel plodders, twin-screw kneading machines and the like and that the term "mechanically worked" is employed herein to describe such milling and/or extrusion. The final product may be in bar form, or in flake or ribbon form, or in other forms such as threads of spaghetti-like noodles, depending upon the size and shape of the extrusion orifice.

Since our invention is concerned in part with heretofore unrecognized, crystalline plasticizable inorganic complexes, we shall first describe the properties and methods of preparation of these complexes. We have been able to produce such complexes using the following four systems: potassium tripolyphosphate-sodium sulfate, potassium tripolyphosphate-potassium sulfate, sodium tri-

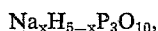
polyphosphate-potassium sulfate, and sodium tripolyphosphate-sodium sulfate. Attempts to ascertain the exact physical structure and chemical composition of the complexes have been handicapped by difficulties in obtaining absolutely pure preparations. Preparations have been obtained using the sodium tripolyphosphate-sodium sulfate system, however, in which the complex was the only crystalline material present, the remainder of the preparation consisting of amorphous material. We therefore have been able to determine the X-ray diffraction pattern of the pure sodium sulfate-sodium tripolyphosphate complex, and this pattern is reproduced in the drawing. Copper $K\alpha_1$ radiation ($\lambda=1.54050$ A.) was used in the determination of this pattern.

The X-ray diffraction pattern shown in the drawing can be characterized by the spacings of the strong diffraction lines at the following approximate values of the angle 2θ : 18.9° , 22.8° , 25.4° , 31.9° , 33.2° and 46.7° . These values of the angle 2θ correspond respectively to the following values of interplanar spacing d : 4.69 A., 3.90 A., 3.50 A., 2.80 A., 2.70 A. and 1.94 A.

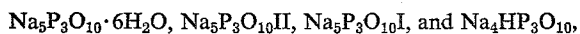
X-ray diffraction studies have been made on all of the sodium and/or potassium systems hereinbefore described and in each case there was a disappearance of some of the X-ray diffraction lines characteristic of the individual components of each system. The disappearance of characteristic lines, in conjunction with the appearance of new lines, indicates the formation of a new crystalline substance. Since we have been able to characterize through X-ray diffraction techniques the sodium-sulfate-sodium tripolyphosphate system, we have found that system to be particularly useful, and much of the discussion which follows is limited in description with reference to that system. However, the other sodium and/or potassium systems hereinbefore described may be readily substituted for the straight sodium system.

It has been found that the X-ray diffraction patterns of different samples of complex may vary in intensity, although the spacings of the strong diffraction lines will be identical. This is caused by the presence of non-crystalline complex or complex having poorly crystallized or strained crystals which alter the absolute line intensities, background intensities, and line shapes of the diffraction patterns.

A crystalline plasticizable inorganic complex can be made by roll drying or spray drying aqueous solutions



containing 5 to 40% of dissolved Na_2SO_4 and wherein x is a value in the range of from 4 to 5, with the optimum ratio of Na_2SO_4 to $Na_xH_{5-x}P_3O_{10}$ being initially about 7:3 by moles. The complex has been made using the following tripolyphosphate salts:



and mixtures of the tetrasodium and pentasodium tripolyphosphates such as $Na_{4.5}H_{0.5}P_3O_{10}$.

The degree of co-crystallization of sodium sulfate and $Na_xH_{5-x}P_3O_{10}$ is greatly influenced by drying rate. When roll drying is employed, considerable amounts of complex are formed with a drying time of one minute. When the drying time is increased to 10 or 15 minutes only moderate amounts of complex are formed. However, a drying time of 22 minutes results in the formation of relatively minor amounts of complex, and no complex is formed when the drying time is increased to 40 minutes. It is apparent from the above that the mixture must be dried rapidly, i.e. the drying time should not exceed about 5 minutes and preferably will not exceed about one minute. The word "drying" is intended to mean the driving off of water until the inorganic constituents have substantially entirely crystallized from solution to form the complex.

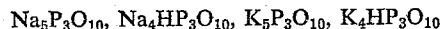
In addition to the roll and spray drying methods, the complex can be made by rapid precipitation of the salts

from solution. Formation of the complex by this precipitation method, of interest mainly as a means of studying the complex, may be described as follows: A fresh aqueous solution containing 40% dissolved



in a 7:3 molar ratio is poured suddenly into a 5 to 20 fold larger volume of very hot ethylene glycol, so that the final mixture is at 230° F. or higher. The precipitate is formed very rapidly and can be filtered off so quickly that the inorganic ingredients need not be hot for more than a minute or two and excessive hydrolysis of the tripolyphosphate will not occur.

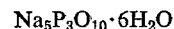
The mechanically worked, substantially non-soap detergent compositions of the present invention contain as essential ingredients at least one water-soluble anionic synthetic sulfate or sulfonate detergent and, as an inorganic builder, one or more of the following crystalline complex inorganic salts: sodium tripolyphosphate-sodium sulfate, sodium tripolyphosphate-potassium sulfate, potassium tripolyphosphate-potassium sulfate, and potassium tripolyphosphate-sodium sulfate. This complex is an essential component of milled synthetic detergent compositions which without this component would have insufficient plasticity to form a coherent milled product. The complex can be further defined as being of a tripolyphosphate salt chosen from



and mixtures of any of these and of an inorganic sulfate salt chosen from Na_2SO_4 and K_2SO_4 . The sodium tripolyphosphate-sodium sulfate inorganic builder will have the X-ray diffraction pattern set forth in the drawing. Although this pattern usually will be superimposed on other patterns, the presence of the complex may nevertheless be determined without difficulty by those skilled in the art.

In the practice of this invention we utilize these inorganic builders, converted to their plastic states, for the manufacture of non-curling, non-cracking, non-brittle milled detergent flakes, as well as other milled or extruded detergent products such as bars or cakes. A process for making milled flakes may be described as follows.

To a crutcher are added at least one water-soluble anionic synthetic sulfate or sulfonate detergent, sodium sulfate (taking into account any sodium sulfate which accompanies the anionic detergent by reason of a neutralization step), and a sodium salt of a tripolyphosphate or a mixture of tripolyphosphates having the following general formula $Na_xH_{5-x}P_3O_{10}$, wherein x is a value in the range of from 4 to 5. Water is then added to the crutcher mixture in an amount sufficient to put the inorganic constituents substantially entirely into solution, when sufficiently warmed and agitated. The inorganic constituents, and particularly the tripolyphosphates, should be in solution. High moisture content of the paste minimizes the formation of suspended



crystals prior to the drying step. These crystals render a portion of the tripolyphosphate unavailable for co-crystallization with sodium sulfate, and this co-crystallization is essential for formation of the complex. If the crutcher mixture which is to be dried contains undissolved sodium sulfate or $Na_xH_{5-x}P_3O_{10}$, the product obtained upon drying will contain in addition to the $Na_5P_3O_{10} \cdot 6H_2O$, other undesirable crystal species such as Na_2SO_4 , $Na_5P_3O_{10}$ and $Na_4P_3O_7$. These suspended crystals have an adverse effect upon the subsequent mechanical working of the detergent compositions. In order to aid in the solution and admixture of the ingredients comprising the crutcher mixture, the mixture is generally heated, although this operation is not essential. We have employed temperatures in the range of from

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about 70° F. to about 180° F., and we prefer to heat the crutcher mixture to a temperature of from about 160° F. to about 180° F. If the crutcher mixture is held at too high a temperature for too long a period of time, the tripolyphosphates may hydrolyze to form pyrophosphate and orthophosphate, neither of which will combine with sodium sulfate to form a plasticizable complex. We have been unable to obtain a plasticizable complex using sodium sulfate in combination with any one of the following phosphates: Na_2HPO_4 , $\text{Na}_3\text{HP}_2\text{O}_7$, and $\text{Na}_4\text{P}_2\text{O}_7$.

The next step involves drying the crutcher mixture as rapidly as possible to promote co-crystallization of the sodium sulfate and $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$. Roll drying and spray drying are both satisfactory; however, slow drying methods such as tunnel drying are not satisfactory, since exposure of the tripolyphosphate in the presence of water to elevated temperatures for extended periods of time results in excessive hydrolysis of the tripolyphosphate. Even under the most carefully controlled conditions as much as 20% of the tripolyphosphate may be lost by hydrolysis. Using a roll drying technique, we prefer to employ steam pressures of 12-30 pounds per square inch gage. Using a spray drying technique we prefer that the exit air temperature be from about 200° F. to about 275° F. It has been observed that the complex in the dry state is unstable at temperatures of 425° F. and above.

There are two alternatives which may be pursued following the drying step. The stock can be continuously fed to mechanical working equipment or it can be stored and at a later time be mechanically worked. Continuous operation is preferable since frequently a large part of the amorphous acid impurities which are formed by hydrolysis of the tripolyphosphate crystallize out as a result of exposure of the product to the atmosphere (e.g. crystalline $\text{Na}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$), without, however, affecting the amount of complex present. There may also be an increase in the crystal size of the crystalline complex. In addition, if the stock is held at too high a water content for too long a period of time, the complex may dissociate with the formation of Na_2SO_4 and tripolyphosphate hexahydrate. All of these changes affect the plastic nature of the stock and as a result make mechanical working more difficult and the products formed less satisfactory. This change in the plastic nature of the stock is, at a given temperature, a function of time and moisture level. At room temperature, stock containing 4.5% water becomes increasingly crystalline and difficult to mill after one week; stock at 9% water becomes undesirably crystalline after about one day; at 2-4% water, the stock should be stored no longer than 7 to 10 days. Under usual operating conditions the stock will be stored no longer than one day.

The amount of water initially present in the dried product which is to be mechanically worked will vary considerably depending upon the nature of the synthetic detergent which is used. As noted hereinbefore some synthetic detergents possess some degree of plasticity. As a general proposition, it may be stated that the greater the plasticity of the synthetic detergent, the lower is the percentage of water which the dried product need contain for optimum mechanical working efficiency. For example, if the active synthetic detergent consists of alkyl benzene sulfonate, which possesses a relatively high degree of plasticity, the initial water level could be reduced to as low as about 2% by weight of total product. However, if the active synthetic detergent is relatively devoid of plasticity (e.g. alkyl glyceryl ether sulfonate) an initial water level as high as 12% by weight of total product may be necessary. Furthermore, the suitable water level range will vary depending upon the type of mechanical working equipment which is employed, the duration of mechanical working, and the temperature of

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the product during mechanical working. Generally the dried product will contain initially from about 6% to about 10% by weight of water.

These stocks at any moisture level have no plasticity under ordinary storage conditions. Temperature adjustment to above 100° F. and preferably in the range of from about 110° F. to about 130° F. usually brings the stock into a plastic state such that it may easily be mechanically worked into flake form. However, because of the inherent plasticity of certain synthetic detergents, especially within certain temperature ranges which vary with individual detergents, the optimum temperature is to some extent dependent on the synthetic detergent present in the composition.

When the stock is fed continuously to the mechanical working equipment directly from the driers, a moisture and temperature adjustment is made, if the stock is not already within the desired ranges.

The final step in the manufacture of the milled flake which comprises a part of the present invention is the mechanical working of the plastic stock. Assuming no pretreatment other than moisture and temperature adjustment, double milling is desirable to produce a well milled uniform flake. One milling step may be omitted by plodding the stock prior to milling. To maintain stock plasticity it is preferred that the surface temperatures of the first rolls be at about from 110° F. to 130° F. The temperature on the first rolls can be as high as about 175° F. if there is sufficient cooling on the last roll to prevent the cut flakes from deforming. Removing cut flakes from the mills requires a shift from the plastic-sticky range to a non-plastic, or semi-plastic, non-sticky range. This may be accomplished on the flake surface by reducing the surface temperature of the last roll to about 70° F., when the temperatures of the first rolls are in the range of 110° F. to 130° F. The temperature of the last roll may have to be as low as 50° F. when the temperature of first rolls substantially exceeds 130° F.

Water soluble salts of sulfonic acids which exhibit detergent effect, such as the higher alkylated benzene sulfonic acids (e.g. sodium salt of the sulfonic acid derived from the condensation product of benzene and a chlorinated kerosene fraction containing predominantly twelve carbon atoms per molecule, or the sodium salt of the sulfonic acid derived from the condensation product of benzene and polypropylenes having from 9 to 15 carbon atoms and averaging 12 carbon atoms) may be employed in the practice of the invention. Also, water-soluble salts of higher mono fatty acid esters of 1,2-dihydroxypropane-3-sulfonic acid (sodium salt of the coconut oil fatty acid monoester of this sulfonic acid is a specific example) will find use in the practice of this invention. In addition, water-soluble salts of higher fatty acid monoesters of lower molecular weight hydroxy alkyl sulfonic acids (e.g. oleic acid ester of the sodium salt of isethionic acid) and of the higher fatty acid amides of lower molecular alkyl sulfonic acids (e.g. ammonium salt of oleic acid amide of N-methyl taurine) may be employed. Likewise, mechanically worked detergent compositions containing large amounts of inorganic salts may be prepared from synthetic detergents such as the water-soluble salts of the higher alcohol esters of sulfoacetic acids. (e.g. sodium salt of the lauryl alcohol ester of sulfoacetic acid), ethers of high molecular alcohols and lower hydroxy sulfonic acids (e.g. monolauryl ether of 1,2-dihydroxy propane-3-sodium sulfonate), and the water soluble alkyl glyceryl ether sulfonates in which the alkyl group contains from 10 to 18 carbon atoms (e.g. the sulfonated and neutralized reaction product obtained by reacting epichlorohydrin and coconut fatty alcohols containing from 10 to 18 carbon atoms).

Other synthetic detergents which are useful in the practice of our invention include the water-soluble salts of high molecular aliphatic sulfuric acid esters such as the alkali metal, ammonium and substituted ammonium salts

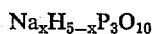
of sulfuric acid esters of normal primary aliphatic alcohols having twelve to eighteen carbon atoms, particularly those whose principal active ingredient is a water-soluble salt of lauryl sulfuric acid or oleyl sulfuric acid. Specific examples are the sodium alkyl sulfate obtained from the mixed higher alcohols produced by the reduction of coconut oil, palm kernel oil, or other oils of the coconut oil group (a group of tropical nut oils characterized by their high content of combined fatty acids having from ten to fourteen carbon atoms) tallow or sperm oil. Also, water-soluble salts of sulfuric acid esters of higher fatty acid monoglycerides (e.g. sodium salt of the coconut oil fatty acid monoester of 1,2-dihydroxy propane-3-sulfuric acid ester) and of the sulfated higher fatty acid alkylolamides (e.g. sodium salt of sulfated coconut oil fatty acid ethanolamide) may be employed. Included among these synthetic detergents are the water-soluble salts of higher alkyl polyethylene oxide sulfuric acid esters (e.g. the sulfated and neutralized reaction product of about three moles of ethylene oxide with one mole of the higher alcohols produced by the reduction of coconut oil fatty acids having 10 to 14 carbon atoms).

These sulfate and sulfonate detergents may be used singly or in combination in the practice of the present invention. The above examples are merely specific illustrations of the numerous detergents which can be incorporated into milled detergent compositions in the presence of large amounts of inorganic salts, and are not intended to be limitations.

The molar ratio of Na_2SO_4 to $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$ in the crutcher mix should be in the range of from about 2:1 to about 3:1.

If all of the Na_2SO_4 and $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$, which was originally added to the crutcher, combined to form the complex, the ease of mechanical working and the coherent properties of the final product would be at an optimum. However, the molar ratio of Na_2SO_4 to $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$ in the mechanically worked product will generally not be the same as the molar ratio of the inorganic salts which were put into the crutcher mix, because of the loss of some of the tripolyphosphate by hydrolysis. The experimental work which has been completed indicates that the molar ratio of sodium sulfate to tripolyphosphate in the complex is about 3:1. If a 3:1 ratio is added to the crutcher, there will usually be some free sodium sulfate in the final product, assuming some loss of tripolyphosphate by hydrolysis. We have found that with the normal loss of 20% to 25% of the tripolyphosphate through hydrolysis a molar ratio of sodium sulfate to tripolyphosphate of 7:3 in the crutcher mix often gives a product showing the X-ray diffraction pattern of only the complex with no free sodium sulfate or tripolyphosphate, the hydrolytic decomposition products of the tripolyphosphates usually being amorphous and therefore not showing an X-ray diffraction pattern. As a consequence, a 7:3 molar ratio sodium sulfate to $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$ in the crutcher mix is preferred in the practice of this invention.

In broad terms, the mechanically worked detergent compositions of the present invention contain from about 10% to about 50% by weight, based on total product, of active synthetic detergent and from about 30% to about 70% by weight, based on total product, of sodium sulfate and $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$. Preferably these compositions will contain from about 15% to about 30% by weight of detergent, based on total product, and from about 40% to about 60% by weight of sodium sulfate and $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$, based on total product. Generally, the sum of the active detergent, sodium sulfate, and



will be at least 60% of the total product. The ratio of sodium sulfate to $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$ in the final product will usually range from about 2:1 to 4:1. In order for the composition to have the desired coherence a preponder-

ance of the sodium sulfate and $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$ should be in the form of a complex having the X-ray diffraction pattern shown in the drawing. Ideally, substantially all of the sodium sulfate and tripolyphosphate in the composition will have combined to form the complex in the 3:1 molar ratio of sodium sulfate to $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$, as demonstrated by an X-ray diffraction analysis showing only complex and no uncombined sodium sulfate and tripolyphosphate. Until the complex can be prepared in pure form, i.e. free of all other material either crystalline or non-crystalline for making X-ray calibration curves and its composition proved constant, the amount of complex present in any given detergent composition cannot be determined by direct analysis for complex.

However, it is possible to indirectly analyze quantitatively for the complex by a combination of physical and chemical analyses for the alkali metal sulfate which is one of the components of the complex.

This indirect analytical technique will be described with reference to the sodium-sulfate-sodium tripolyphosphate complex system. Chemical analyses can be made for total Na_2SO_4 in any given preparation, and such methods of analysis are well known to those skilled in the art. It is reasonable to assume that any uncomplexed Na_2SO_4 will exist as free Na_2SO_4 , and in the preparations of the present invention virtually all of this Na_2SO_4 will exist in the crystalline state as $\text{Na}_2\text{SO}_4\text{V}$. X-ray diffraction quantitative analytical techniques have been employed for the quantitative analysis of uncomplexed $\text{Na}_2\text{SO}_4\text{V}$ in the presence of sodium tripolyphosphate.

All X-ray diffraction analyses were accomplished with a Geiger counter powder diffractometer which measures and records the relative intensities of the diffraction lines. Copper $\text{K}\alpha_1$ radiation ($\lambda=1.54050 \text{ \AA}$) was used. This diffractometer is a parafocusing X-ray diffraction device which utilizes a Geiger counter for directly measuring the intensity diffracted at any particular angle 2θ . A complete description of this device may be found in "X-ray Diffraction Procedures," Klug and Alexander, published by John Wiley and Sons, Inc., New York City, 1954, at page 235. By means of this device, the intensity diffracted at the various 2θ values can be shown as a line graph.

The procedure which can be used for measuring the amounts of $\text{Na}_2\text{SO}_4\text{V}$ present in a given preparation can be adapted from the one set forth by Klug and Alexander (op. cit.) beginning at p. 422. In this procedure, an internal standard is mixed with $\text{Na}_2\text{SO}_4\text{V}$, in a fixed proportion.

Magnesium oxide has proved to be a satisfactory internal standard for use in quantitative determination of the free $\text{Na}_2\text{SO}_4\text{V}$ in a preparation which contained tripolyphosphate, and the diffraction line at a spacing of 2.11 \AA . ($42.9^\circ 2\theta$) produced by the magnesium oxide was selected for measuring the intensity ratio of $\text{Na}_2\text{SO}_4\text{V}$ to the internal standard.

The amount of $\text{Na}_2\text{SO}_4\text{V}$ present in a preparation is determined using the diffraction line intensity at a spacing of 3.20 \AA . ($28.1^\circ 2\theta$).

The difference between total sodium sulfate, as determined chemically, and uncombined sodium sulfate, as determined by X-ray diffraction analysis, represents the sodium sulfate which is complexed with sodium tripolyphosphate in the 3:1 molar ratio.

It is common to employ various auxiliary materials in synthetic detergent compositions. The detergent compositions of the present invention may include any of these substances employed by the art in admixture with such detergent compositions generally, provided that the use of any such materials does not adversely affect the plastic properties of the mix during the mechanical working step. These auxiliary materials may be inorganic or organic in structure and may be mixed with the active detergent and plasticizable complex in any suitable manner. Such conventional inorganic auxiliary materials as the alkali metal silicates, chlorides, carbonates, the alkali metal

phosphates (e.g. metaphosphate, pyrophosphate, orthophosphate), etc. may be employed in these compositions. Suitable organic materials may be added, such as glycerol, carboxymethylcellulose, organic suds builders (such as coconut ethanalamide, i.e. the monoethanol amide of coconut oil fatty acids), tarnish inhibitors, fluorescent brightening agents, perfumes, coloring matter etc. The addition of soap to the synthetic detergent compositions is not essential to provide these compositions with the plasticity necessary for mechanical working. The inorganic complex by itself provides sufficient plasticity. However, it may be desirable that soap be present in the synthetic detergent compositions of this invention as a supplemental and less expensive washing agent and as a low temperature sudsing agent.

The stability of compositions made according to this invention is truly remarkable, even after extended periods of time. It would normally be expected that detergent flakes containing up to 60% of inorganic salts would, after a period of time, crack, crumble, acquire a hard crystalline feel, and lose whatever coherent properties they might have originally possessed. However, the detergent flake compositions of this invention after ageing for up to two years still retain their original form, waxy feel, and glossy appearance. Furthermore, the brittleness of these flakes is about equal to that of substantially pure mechanically worked soap flakes stored under similar conditions for the same period of time.

The following examples are additionally illustrative of the nature of the present invention, and it will be understood that the invention is not limited thereto.

Example I

A detergent composition is prepared by crutching at 170° F. about a 40% solids water solution containing on a solids basis, about 30% pentasodium tripolyphosphate, 33.5% sodium sulfate, 6% sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O}$, 1.6), 1.6% sodium chloride, 10% alkyl glyceryl ether sulfonate (the sulfonated and neutralized product obtained by reacting epichlorohydrin and coconut fatty alcohols containing 10 to 14 carbon atoms), 10% tallow alkyl sulfate (the sodium alkyl sulfate obtained from the mixed higher alcohols produced by the reduction of tallow), 4% coconut ethanalamide (the monoethanolamide of coconut oil fatty acids), 4% of the sodium soap derived from castor oil, and 0.4% glycerol. The solution is roll dried for five minutes using steam pressure of 25 pounds per square inch, gage. The resulting composition which contains about 8% water by weight, is adjusted in temperature to 130° F. and extruded through a pellet-forming plodder. The extruded stock is then put through a three roll milling device with the surface temperature of the first rolls being 120° F. and the surface temperature of the final roll being 75° F. The cooled non-plastic, non-sticky sheets are then cut into ribbons and these ribbons into flakes as they are removed from the rolls.

If the product is desired in bar form rather than flake form it is unnecessary to cool the final roll below 100° F. The milled detergent composition coming from the final roll may be fed to a plodder, extruded in continuous bar form, cut into individual cakes, stamped (or pressed) into desired shape and pattern and the cakes wrapped and packed; or the milling may be omitted altogether and the bar formed by simply extruding the crutcher mix in bar form.

Example II

A detergent composition is prepared by crutching at 180° F. about a 30% solids water solution containing on a solids basis about 35% pentasodium tripolyphosphate, 31% sodium sulfate, 14% alkyl glyceryl ether sulfonate (the sulfonated and neutralized reaction product obtained by reacting epichlorohydrin and coconut fatty alcohols containing 10 to 15 carbon atoms), 14% tallow

alkyl sulfate (the sodium alkyl sulfate obtained from the mixed higher alcohols produced by the reduction of tallow), and 6% of the sodium soap derived from castor oil. The crutcher mixture is then spray dried to a moisture level of about 5% by weight of the product, the exit air temperature being 250° F. The moisture level of the spray dried product is then adjusted to 7% by weight of the product, and the temperature is adjusted to 110° F. This product is then put through a three roll mill with the surface temperature of the first rolls being 110° F. and the surface temperature of the final roll being 75° F. This milling operation is then repeated under the same temperature conditions. The cooled non-plastic, non-sticky sheets are then cut into ribbons and these cut into flakes and the flakes removed from the rolls.

The following are examples of mechanically worked dried detergent compositions which can be obtained in flake, ribbon, or bar form by the process of the present invention as described in either of the preceding examples.

Example III

	Percent
Sodium coconut alkyl sulfate (the sulfated and neutralized product obtained from the mixed higher alcohols produced by the reduction of coconut oil fatty acids having 10 to 14 carbon atoms) ---	15
Alkyl benzene sulfonate (the sodium salt of the sulfonic acid derived from the condensation product of benzene and polypropylenes having from 9 to 15 carbon atoms and averaging 12 carbon atoms) -----	20
$\text{Na}_4\text{HP}_3\text{O}_{10}$ -----	23
Sodium sulfate -----	20
Coconut ethanalamide (same as in Example I) ----	4
Sodium silicate -----	6
Sodium chloride -----	4
Water -----	8

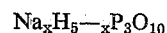
Example IV

	Percent
Alkyl glyceryl ether sulfonate (the sulfonated and neutralized reaction product obtained by reacting epichlorohydrin and coconut fatty alcohols containing 10 to 14 carbon atoms) -----	18
$\text{Na}_5\text{P}_3\text{O}_{10}$ -----	29
Sodium sulfate -----	30
Sodium soap of castor oil -----	4.6
Coconut ethanalamide (same as in Example I) --	4
Sodium chloride -----	6
Glycerine -----	0.4
Water -----	8

An equivalent amount of potassium sulfate can replace the sodium sulfate in this example and/or an equivalent amount of $\text{K}_5\text{P}_3\text{O}_{10}$ can replace the $\text{Na}_5\text{P}_3\text{O}_{10}$.

Having thus described our invention, what we claim is:

1. In the process of making a coherent mechanically worked synthetic detergent composition from ingredients comprising essentially, water, sodium sulfate,



wherein x is a value in the range of from 4 to 5, and at least one water-soluble anionic synthetic organic detergent salt selected from the group consisting of anionic sulfate and sulfonate synthetic detergents, the steps which comprise: (1) blending a mixture of water, from about 10% to about 50% by weight of total solids of said synthetic detergent salt, and from about 30% to about 70% by weight of total solids of said sodium sulfate and $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$, the molar ratio of sodium sulfate to $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$ being from about 2:1 to about 3:1 and the water content being such that the inorganic constituents are substantially entirely in solution, (2) drying the mixture until said inorganic constituents have substantially entirely crystallized from solution and over a

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period of time not exceeding about five minutes, thereby promoting co-crystallization of the sodium sulfate and $\text{Na}_x\text{H}_5-x\text{P}_3\text{O}_{10}$ to form a complex having an X-ray diffraction pattern corresponding to that shown in the drawing characterized by strong diffraction line values of the angle 2θ of 18.9° , 22.8° , 25.4° , 31.9° , 33.2° and 46.7° , and (3) thereafter mechanically working the mixture at an initial water content of from about 2% to about 12% by weight of total product and at a temperature of from about 50°F. to about 175°F. , said water level and temperature being such that the mixture can be effectively mechanically worked as a plastic coherent mass.

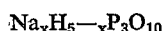
2. The process of claim 1 in which the molar ratio of sodium sulfate to $\text{Na}_x\text{H}_5-x\text{P}_3\text{O}_{10}$ in step 1 is about 7:3.

3. The process of claim 1 in which the molar ratio of sodium sulfate to $\text{Na}_x\text{H}_5-x\text{P}_3\text{O}_{10}$ in step 1 is from about 2:1 to about 3:1 and the water level in step 3 is from about 6% to about 10% by weight of total product.

4. The process of claim 1 in which the molar ratio of sodium sulfate to $\text{Na}_x\text{H}_5-x\text{P}_3\text{O}_{10}$ in step 1 is from about 2:1 to about 3:1, the water level in step 3 is from about 6% to about 10% by weight of total product and the temperature in step 3 is from about 110°F. to about 130°F.

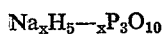
5. The process of claim 1 in which the molar ratio of sodium sulfate to $\text{Na}_x\text{H}_5-x\text{P}_3\text{O}_{10}$ in step 1 is from about 2:1 to about 3:1, the water level in step 3 is from about 6% to about 10%, by weight of total product, the temperature in step 3 is from about 110°F. to about 130°F. , and the detergent salt consists of approximately equal parts by weight of the sulfated and neutralized fatty alcohols produced by the reduction of tallow and alkyl glyceryl ether sulfonate wherein the alkyl group contains from 10 to 18 carbon atoms.

6. In the process of making a coherent mechanically worked synthetic detergent composition from ingredients comprising essentially water, sodium sulfate,



wherein x is a value in the range of from 4 to 5, and water soluble anionic synthetic organic detergent salts comprising approximately equal parts by weight of the sulfated and neutralized fatty alcohols produced by the reduction of tallow and alkyl glyceryl ether sulfonate wherein the alkyl group contains from 10 to 18 carbon atoms, the steps which comprise: (1) blending a mixture of from about 15% to about 30% by weight of total solids of said synthetic detergent salts, from about 40% to about 60% by weight of total solids of said sodium sulfate and $\text{Na}_x\text{H}_5-x\text{P}_3\text{O}_{10}$, and an amount of water such that the inorganic constituents are substantially entirely in solution, the molar ratio of sodium sulfate to $\text{Na}_x\text{H}_5-x\text{P}_3\text{O}_{10}$ being about 7:3, (2) drying the mixture until said inorganic constituents have substantially entirely crystallized from solution and over a period of time not exceeding about one minute, thereby promoting co-crystallization of the sodium sulfate and $\text{Na}_x\text{H}_5-x\text{P}_3\text{O}_{10}$ to form a complex having an X-ray diffraction pattern corresponding to that shown in the drawing characterized by strong diffraction line values of the angle 2θ of 18.9° , 22.8° , 25.4° , 31.9° , 33.2° and 46.7° , and (3) thereafter mechanically working the mixture as a plastic coherent mass at an initial water level of from about 6% to about 10% by weight of total product and at a temperature of from about 110°F. to about 130°F.

7. A coherent mechanically worked synthetic detergent composition comprising essentially from about 10% to about 50% of at least one detergent salt selected from the group consisting of water soluble synthetic organic sulfate and sulfonate detergents and from about 30% to about 70% of inorganic salts consisting of Na_2SO_4 and



wherein x is a value in the range of from 4 to 5, within the molar ratio range of 2:1 to 4:1, with a preponderance of

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the inorganic salts being in the form of a complex having an X-ray diffraction pattern characterized by strong diffraction line values of the angle 2θ of 18.9° , 22.8° , 25.4° , 31.9° , 33.2° and 46.7° as shown in the drawing, said complex having a molar ratio of said inorganic sulfate to phosphate salts of about 3:1, and the above percentages being by weight of the total product, said values of the angle 2θ corresponding respectively to values of interplanar spacing d of 4.69 A., 3.90 A., 3.50 A., 2.80 A., 2.70 A. and 1.94 A.

8. A coherent mechanically worked synthetic detergent composition comprising essentially from about 10% to about 50% of at least one detergent salt selected from the group consisting of water soluble synthetic organic sulfate and sulfonate detergents and from about 30% to about 70% of inorganic salts consisting of Na_2SO_4 and $\text{Na}_x\text{H}_5-x\text{P}_3\text{O}_{10}$, wherein x is a value in the range of from 4 to 5, within a molar ratio range of 2:1 to 4:1, the sum of the said detergent salt and inorganic salts being at least 60% of the total product and a preponderance of the inorganic salts being in the form of a complex which exhibits an X-ray diffraction pattern characterized by strong diffraction line values of the angle 2θ of 18.9° , 22.8° , 25.4° , 31.9° , 33.2° and 46.7° as shown in the drawing, said complex having a molar ratio of said inorganic sulfate to phosphate salts of about 3:1, the above percentages being by weight of total product, said values of the angle 2θ corresponding respectively to values of interplanar spacing d of 4.69 A., 3.90 A., 3.50 A., 2.80 A., 2.70 A. and 1.94 A.

9. A coherent mechanically worked synthetic detergent composition comprising essentially from about 15% to about 30% of at least one detergent salt selected from the group consisting of water soluble synthetic organic sulfate and sulfonate detergents and from about 40% to about 60% of inorganic salts consisting of Na_2SO_4 and $\text{Na}_x\text{H}_5-x\text{P}_3\text{O}_{10}$, wherein x is a value in the range of from 4 to 5, in a molar ratio of about 3:1, substantially all of said inorganic salts being in the form of a complex having an X-ray diffraction pattern characterized by strong diffraction line values of the angle 2θ of 18.9° , 22.8° , 25.4° , 31.9° , 33.2° , and 46.7° as shown in the drawing, the above percentages being by weight of total product, said values of the angle 2θ corresponding respectively to values of interplanar spacing d of 4.69 A., 3.90 A., 3.50 A., 2.80 A., 2.70 A. and 1.94 A.

10. The composition of claim 9 in which said detergent salt comprises approximately equal parts by weight of the sulfated and neutralized fatty alcohols produced by the reduction of tallow and alkyl glyceryl ether sulfonate wherein the alkyl group contains from 10 to 18 carbon atoms.

11. In the process of making a coherent mechanically worked synthetic detergent composition from ingredients comprising essentially, water, an inorganic sulfate salt selected from the group consisting of Na_2SO_4 and K_2SO_4 , an inorganic tripolyphosphate salt selected from the group consisting of $\text{Na}_5\text{P}_3\text{O}_{10}$, $\text{Na}_4\text{HP}_3\text{O}_{10}$, $\text{K}_5\text{P}_3\text{O}_{10}$, $\text{K}_4\text{HP}_3\text{O}_{10}$ and mixtures of any of these, and at least one water-soluble anionic synthetic organic detergent salt selected from the group consisting of anionic sulfate and sulfonate synthetic detergents, the steps which comprise: (1) blending a mixture of water, from about 10% to about 50% by weight of total solids of said synthetic detergent salt, and from about 30% to about 70% by weight of total solids of said sulfate salt and said tripolyphosphate salt, the molar ratio of sulfate salt to tripolyphosphate salt being from about 2:1 to about 3:1 and the water content being such that the inorganic constituents are substantially entirely in solution, (2) drying the mixture until said inorganic constituents have substantially entirely crystallized from solution and over a period of time not exceeding about five minutes, thereby promoting co-crystallization of the sulfate salt and tripolyphosphate salt

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to form a crystalline plasticizable complex, and (3) thereafter mechanically working the mixture at an initial water content of from about 2% to about 12% by weight of total product and at a temperature of from about 50° F. to about 175° F., said water level and temperature being such that the mixture can be effectively mechanically worked as a plastic coherent mass.

14**References Cited in the file of this patent****UNITED STATES PATENTS**

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,941,948

June 21, 1960

Joseph Blinka et al.

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

Column 3, line 48, strike out "containing 5 to 40% of dissolved Na_2SO_4 and" and insert the same after "aqueous solutions", in line 46, same column; column 9, line 74, for "epichlorophydrin" read -- epichlorohydrin --; columns 10 to 12, in all of the claims, wherever the formula " $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$ " appears, read -- $\text{Na}_x\text{H}_{5-x}\text{P}_3\text{O}_{10}$ --.

Signed and sealed this 25th day of April 1961.

(SEAL)

Attest:

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Commissioner of Patents