PROCESS FOR MAKING DETERGENT TABLET

Albert Lyle Schuerad, Nutley, N.J., assignor to Colgate-Palmolive Company, New York, N.Y., a corporation of Delaware

No Drawing. Filed Apr. 3, 1961, Ser. No. 160,033
5 5 Claims. (Cl. 252—138)

The present invention relates to a detergent tablet which is resistant to abrasion and accidental breakage when dry and is also adequately disintegratable in water in normal laundering operations. The invention includes a process for making such a tablet by coating solid detergent particles with soluble and insoluble silicate compounds, lightly compacting the coated particles to a forming tablet, and applying to the surface of the tablet a coating of readily water soluble film-forming organic synthetic polymer.

It has been found that the production of detergent tablets from particulate detergent compositions comprising nonionic detergents can be facilitated and the product can be improved by the processes herein described. In accordance with the invention, a process for making a briquetted detergent tablet begins with mixing together water soluble nonionic organic detergent with a normally solid water soluble inorganic salt and producing therefrom a particulate detergent containing up to 21% moisture. To the particles an aqueous solution of soluble silicate is applied, preferably by spraying. The silicate coating is 3 to 20% of the product and the moisture content of the detergent is raised to about 16 to 25% by the silicate solution. Next, to the coated detergent particles 0.5 to 5% of finely divided water insoluble inorganic siliceous material, such as a silicate, is applied to form another coating, held to the particles by the water soluble silicate. The detergent particles are subsequently pressed into a solid form retaining briequetting table at a pressure low enough to form a tablet which is readily disintegratable in water, after which about 25 to 50% of a readily water soluble synthetic organic film-forming polymer is applied to the tablet to form on the surface thereof a water soluble film which is of strength sufficient to help make the detergent tablet resistant to abrasion and accidental breakage, when dry, and of solubility such that the detergent tablet is readily disintegratable in water.

In following the inventive process, it is preferred to mix together the major constituents of a heavy duty synthetic organic detergent composition, including nonionic detergent and inorganic builder salts, in an aqueous solution or dispersion, usually containing 20-70% solids. The uniform slurry is atomized and sprayed into a heated drying tower to form a spray dried detergent in particulate form, preferably of the "low-sudsing" type formula. Instead of spray drying, other production techniques may be employed to produce such detergent powders.

The dry or partially dried detergent is agitated, as by tumbling in a rotating inclined drum and while being so moved is sprayed with a solution of water soluble silicate. The silicate is spread over the surfaces of the particles by the tumbling action and causes the finer particles present to adhere to others to form particles of larger size. This agglomeration is often accompanied by a decrease in density. In addition to altering product density, the silicate conditions the particles so that they will adhere together better in subsequent briquetting operations.

After coating with silicate and continuing mixing for about one to five minutes, a finely divided water insoluble silicate powder, preferably talc, that will pass a 200 mesh sieve, is distributed over the particles previously coated with soluble silicate. The talc coating tends to arrest agglomeration and improves the ease of pressing into briquettes. The talc is preferably applied in the same mixing drum or vessel as the silicate, preferably as a fluidized powder blown into the mixer by air pressure. After about 5 to 15 minutes' mixing the treated detergent particles are withdrawn, oversized agglomerates screened out and the product, preferably agglomerates of particle size within the range of 6 to 60 mesh is removed. The coating process described above may be either of the batch type or continuous, the latter being preferred for high speed commercial procedures.

The coated detergent may be immediately pressed into briquetted tablet form or may be temporarily stored for several hours before compaction. The free flowing particles are fed to mold cavities and are lightly compacted to desired shape, at a pressure of about 10 to 100 pounds per square inch, preferably about 40 to 90 pounds per square inch. The pressure employed is that at which the tablets made are resistant to abrasion and accidental breakage, when dry, and are still readily disintegratable in water. Thus, in a simulated washing machine test, freshly made tablets, also coated with organic polymer as discussed below, should disintegrate in agitated water at room temperature in less than 90 seconds, preferably less than 50 seconds. When aged, the hardened tablets may take as long as 4 minutes to break up completely. Although it is desirable to have the most rapid solubility characteristics possible, even the aged tablets still dissolve fast enough in usual laundry usage to wash satisfactorily.

The lightly compacted tablets are next sprayed with a protective coating of an organic film-forming polymer, preferably polyvinyl alcohol, usually as an aqueous solution applied in spray form. The entire briquette surface is covered and a strong bond between polyvinyl alcohol and the previous coating of soluble silicate and talc is obtained. To speed production and make a hard protective coating on the detergent tablet, the polyvinyl alcohol coating is dried by infra-red heating lamps. The finished briquettes are then packed in plastic bags or sleeves, boxed, cased and shipped.

The products made according to this invention are strong and can withstand rigid shipping and handling tests without objectionable breakage occurring. Yet, the tablets disintegrate readily in water.

The materials of the present compositions and the processing operations will now be described in greater detail to enable one of skill in this art better to appreciate the significance of the invention.

The water soluble nonionic detergent is preferably an alkyl phenoxypolymer lower alkyl lower alkanol and nonyl phenoxypolyoxyethylene alcohol of about 9 to 10 ethoxy groups is a specific example of this group found to be excellent. In the preferred class of compounds mentioned the alkyl group is usually of 6 to 14 carbon atoms and the alkyloxy chain is of 4 to 12 units long, each unit comprising from 2 to 4 carbon atoms. Commercial products of this type are usually mixtures and may be used in addition to the alkyl phenoxypolyoxyethylene alkanol and in some cases in replacement thereof. In the present detergent compositions the proportion of nonionic detergent, on a final product weight basis, as are all other
proportions given, is usually 4 to 14%, preferably 7 to 12%.

In addition to nonionic detergent an anionic organic detergent may also be present, usually primarily to produce some foam and to contribute its cleaning power to the composition. A preferred detergent is sodium tridecyl benzene sulfonate, a mixture of sodium alkyl benzene sulfonates, which may be derived from alkyl benzene sulfonates, and which may be prepared in other olefinic water-soluble sulfonates. It is a mixture of alkyl benzene sulfonates, the alkyl benzene alkyl sulfonates or aromatic sulfonates, sulfonated organic detergent compounds containing fatty acid or acyl groups of 10–18 carbon atoms, such as sodium lauryl sulfate, sodium coconut oil fatty acids monoglyceride sulfate and sodium salts of higher fatty acid amide of N-methyltaurine. The proportion of anionic detergent should normally be from about 1 to 5%.

A foam stabilizer, such as a long chain fatty compound having an alkyl group of 12 to 18 carbon atoms, preferably a mixture of cetyl and stearyl alcohols, may also be included to thicken the foam of the anionic detergent. Ordinarily 0.5 to 5% and preferably 0.5 to 3% of this material is sufficient.

The inorganic water soluble sodium salt is preferably a builder salt of the polyphosphate type, such as sodium tripolyphosphate. Other useful builders and fillers include alkali metal sulfates, sodium and potassium carbonates, tetrasodium pyrophosphate and sodium silicates of various Na$_2$O/SiO$_2$ ratio. These give the present tablets a useful and functional base for the organic materials. From 30 to 75% of the product may be soluble inorganic salt and preferably about 30% sodium tripolyphosphate is used in mixture with smaller proportions of sodium silicate (Na$_2$O/SiO$_2$ of 1.25:2) and sodium sulfate.

Following the spray drying method mentioned earlier a slurry of the above materials in an aqueous medium is dried to a moisture content of 7 to 14%. By this and other methods, moistures of up to 21%, usually 2 to 18%, are obtainable and particles of such moisture may be made into satisfactory tablets by the present methods. If the spray dried particles are high in fines or coarse pieces, they should be screened or classified to substantially all (90% or more) be held by a 100 mesh sieve (U.S. Standard Series) with none on 6 or 8 micron.

Silicate solution sprayed on the detergent beads while they are being tumbling or otherwise agitated is a water soluble metal silicate. Of the alkali metal silicates the best is sodium silicate of an Na$_2$O/SiO$_2$ ratio from 1:2 to 1:3, most preferably 1:2.35. This silicate is made into an aqueous solution which may be of 25 to 40% solids content. Generally the silica solution will be of 35 to 43.5% solids content, preferably about 35 to 37%. These concentrations can be satisfactorily stored and sprayed. The proportion of water solution of sodium silicate sprayed onto the moving detergent bed surfaces is usually 15 to 30%, preferably about 20% silicate solution. Thus 15 to 30 parts of solution are sprayed onto about 85 to 70 parts of detergent beads, neglecting to make a minor correction of these figures for the small amounts of polyvinyl alcohol or other coating applied later. The 3 to 15% silicate coating, preferably 6.5 to 8.5% helps agglomerate the beads, to a 9- to 60-mesh range (3.0 to 4.25 to 4 millimeter diameters) and helps in creating a strong briquette. It also raises moisture content to 16 to 25%, preferably 17.5 to 20.5% which is often best for briquetting.

After coating with silicate and continuing mixing and agglomerating, the tumbling beads are next coated with very finely divided talc. Other magnesium silicates or other finely divided water insoluble inorganic silicates of equivalent properties may be used with or in place of talc. 0.5 to 5% of talc is sufficient to hinder further agglomerating and improves the speed and ease of briquetting. After the particles are coated with talc they are removed from the tumbling zone and are immediately ready for pressing into tablets.

In pressing, the detergent particles are flowed into molds or pockets in high speed shaping equipment. Opposite dies have the desired shape cut into a cylinder and form it into a flat circular tablet, beveled and with a diametric score line to facilitate breaking in half, if desired. The dies are set with stops to make tablets of a constant thickness so the same volumes of detergent are charged to keep compacting pressures within the correct range of 10 to 100 pounds per square inch.

The pressed tablets, due to their silicate coatings, can be handled without fear of objectionable breakage. However, such tablets would not be permanently satisfactory unless subsequently coated with a water soluble polymeric film forming polymer, such as polyvinyl alcohol. The polyvinyl alcohols of commerce usually contain minor proportions of a lower fatty acid ester, polyvinyl acetate. This may be present in polyvinyl alcohols employed in this invention to the extent of about 10 to 50%. The useful polyvinyl alcohols are also of a weight degree of polymerization between about 30 and 300. A good polyvinyl alcohol for use in accordance with this invention has a weight average degree of polymerization of about 50 to 250 (viscosity of about 2 to 6 centipoises) and a polyvinyl acetate content of 15 to 25% and a most preferred material with a weight average degree of polymerization of about 100 (viscosity of 3.5 centipoises) and polyvinyl acetate content of 20%.

The polyvinyl alcohol should contain relatively little insoluble matter, should be colorless, odor-free and of neutral pH. Deviations from the above requirements may be made where warranted but, in general, the polyvinyl alcohol of the specified specifications would be most acceptable for household detergent products. Instead of the described polyvinyl alcohol, other readily water soluble synthetic organic film-forming polymers of similar properties can be used, but usually other compounds will not be as effective. However, polyvinyl pyrrolidone, sodium carboxymethyl cellulose, hydroxypropyl methyl cellulose and other polymeric substances can produce water soluble films for briquette surfaces. When used, it is preferred to mix them with polyvinyl alcohol so that the special advantages attending the presence of that material may be retained.

Coating of the detergent tablet is preferably done by spraying onto the surfaces a liquid comprising the polyvinyl alcohol dissolved in water. The aqueous solution should be sprayed or atomized in fine droplet form as evenly as practicable onto the surface of the briquette. The spray solution may contain glycerol or other low polyols to serve as plasticizers to help to keep the polyvinyl alcohol flexible and resilient, detergents or wetting agents to improve wetting of the briquette and neutralizing agents, e.g., sodium bicarbonate, to improve the odor of the polyvinyl alcohol by reacting with free acid present. Among other plasticizers that may find use are glycols, e.g., ethylene glycol and sugar alcohols, such as sorbitol.

The amount of polyvinyl alcohol sprayed onto the briquette surface should be from 0.25 to 5% of the briquette weight, preferably 0.3 to 1%. The polyvinyl alcohol is preferably applied in a 10 to 25% solution, such as a 17% solution in water, the proportion of such solutions used being from 3 to 10%, preferably about 6% of the briquette weight. When sprayed onto the detergent briquette surface, the polyvinyl alcohol and its solvent fill the voids between particles and also cover the surfaces of the particles. Because the briquette before coating is not perfectly smooth, it is evident that the coating will be thicker in some spots than in others but it may be said that the average thickness is from 0.01 to 0.8 millimeter, preferably 0.2 to 0.1 millimeter.
After coating with polyvinyl alcohol solution, the briquette may be surface dried by forced air, heated air, infra-red rays or other suitable drying means to remove essentially all the moisture accompanying the polyvinyl alcohol in the coating spray. Thus, the final product will be of about the same moisture content as that obtained in the particles before pressing. After drying, the briquette may be packed immediately in cartons ready for shipment and use. It is usually preferred that such cartons contain moisture barriers to assist in maintaining the correct moisture content in the briquette. Briquettes made in accordance with this invention may be shipped in commerce without breaking and even though stored for months before use will still disintegrate and dissolve rapidly enough when added to the tub of any of the conventional washing machines. They will also pass the rather severe strength and solubility requirements set for such products, withstanding a drop of at least 1 foot onto a hard surface, e.g., a metal plate, without breaking and also disintegrating in agitated water at 100° Fahrenheit in a washing machine within a period of no greater than 4 minutes, usually within one minute. The washing machine referred to is a commercial top-loading machine with a center post agitator of average operating and design characteristics. The following examples illustrate the invention. All percentages and proportions in the examples, this specification and the appended claims are by weight unless otherwise indicated.

**Example I**

Nonyl phenol ethoxylate (9.5 ethylene oxides) 13
Sodium tridecyl benzene sulfonate 5
Technical cetyl alcohol 1
Sodium tripolyphosphate 43
Sodium sulfate 25
Sodium silicate (Na<sub>2</sub>O/SiO<sub>2</sub> ratio of 1:2.35) 4
Moisture 8.5
Adjuvants (anti-redeposition agent, fluorescent brightener, perfume, anti-oxidant) 0.5

100.0

The above formula was made by spray drying an aqueous crutcher mix slurry of all materials except perfume which was added after spraying. In a tumbling drum there were added 100—X parts of spray dried particles of such formula of size from 8 to 100 mesh by spraying the following amounts and concentrations of a water solution of sodium silicate of Na<sub>2</sub>O/SiO<sub>2</sub> ratio of 1:2.35. Moisture contents of briquetted tablets made therefrom are also given:

<table>
<thead>
<tr>
<th>(X) Parts silicate solution</th>
<th>Percentage solids</th>
<th>Final moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>42.5</td>
<td>18.6</td>
</tr>
<tr>
<td>23.7</td>
<td>42.5</td>
<td>20.0</td>
</tr>
<tr>
<td>28.8</td>
<td>38.9</td>
<td>17.6</td>
</tr>
<tr>
<td>32.9</td>
<td>39.0</td>
<td>18.0</td>
</tr>
<tr>
<td>35.9</td>
<td>37.9</td>
<td>18.0</td>
</tr>
<tr>
<td>38.8</td>
<td>37.9</td>
<td>20.0</td>
</tr>
<tr>
<td>41.8</td>
<td>34.7</td>
<td>20.7</td>
</tr>
</tbody>
</table>

After about 5 minutes' tumbling, talc powder, substantially all less than 200 mesh, was air-blown onto the tumbling particles. The amount of talc used was 2% and the beads were agitated for another ten minutes, after which they had been agglomerated to 6 to 60 mesh and were ready for immediate pressing. Within two hours, they were pressed to flat cylinder shape at a pressure within the 40 to 90 pounds per square inch range and spray coated with about 0.8% polyvinyl alcohol in a 17% aqueous solution at about 150° F. The polyvinyl alcohol was of weight average degree of polymerization about 100 and contained 15-25% polyvinyl acetate. After coating of the tablet the polyvinyl alcohol was dried under infra-red lamps. The coating made was of irregular thickness, between about 0.01 and 0.8 millimeter.

The tablets resulting pressed very easily in the automatic machinery employed (having Teflon dies and sleeves) and satisfactorily passed drop tests, shipping tests and disintegration tests (in water). They are attractive in appearance, dust free and easy to use. The polyvinyl alcohol of the coating even increases the anti-redeposition properties of the detergent. In storage, the tablets did not swell or crumble, but retained their original shapes and surface appearances. They could be shipped, even in cold weather, and when packed properly, exhibit a surprisingly good resistance to breakage.

**Example II**

Nonyl phenoxo polyoxyethylene ethanol, having
9.5 oxyethylene groups per molecule 9.3
Sodium higher alkyl benzene sulfonate (alkyl group being a mixture of propylene tetramer and pentamer) 3.7
Higher fatty alcohol (mixtures of C<sub>10</sub> and C<sub>12</sub> alcohols) 0.8
Phosphate solids (from sodium tripolyphosphate) 35.0
Sodium silicate (Na<sub>2</sub>O/SiO<sub>2</sub> ratio of 1:2.35) 3.0
Sodium sulfate 39.0
Sodium carboxymethyl cellulose 0.3
Polyvinyl alcohol 0.1
Adjuvants 0.3
Moisture 8.5

100.0

This formula was made by the spray drying method, as in Example I. The beads were coated with 20 parts of a 43.5% solids water solution of sodium silicate of Na<sub>2</sub>O/SiO<sub>2</sub> ratio of 1:2.35, which raised the moisture content of the beads (and tablet) to 17.7%. The agglomerated beads resulting from tumbling were coated with 25% talc, then pressed and coated with polyvinyl alcohol, as described in Example I. The talc-coated beads pressed easily and the products resulting were good hard detergent tablets which still are lighter in weight than is usual for pressed powders and can be readily dissolved because of their rapid disintegration in water. They pass the earlier described strength and disintegration tests and are good detergents in a very useful pre-measured form.

When the amount of talc used was cut to 1% a decrease in pressing ease resulted but still the tablets could be made more readily without any talc. Hundreds of talc other siliceous insoluble materials may also be used, e.g.,田野s, micas, even silica flour, preferably as only a partial replacement therefor.

The present invention has been illustrated by description of the invented products made and manufacturing methods employed. These examples are illustrative only and are not to be considered as limiting the allowed claims.

What is claimed is:

1. A process for making a briquetted detergent tablet comprising mixing together about 4 to 14% of a water soluble nonionic organic polyethylene detergent selected from the group consisting of ethoxylated alkyl phenol, ethoxylated higher fatty alcohol, ethoxylated higher fatty acid and ethoxylated propylene oxide polymers with about 30 to 75% of a normally solid water soluble inorganic, alkali metal builder salt, producing therefrom a particulate detergent containing up to 21% moisture, applying an aqueous solution of soluble alkali metal silicate to the particulate detergent to coat the particles with 3 to 20% soluble alkali metal silicate to cause agglomeration into larger particles and to increase the moisture content thereof to about 16 to 25%, applying to the coated detergent particles 0.5 to 5% of finely divided water insoluble inorganic silicate to form a coating on the particles, held
3,231,506

7 to them by the water soluble silicate, and to arrest agglomeration of the detergent particles and produce agglomerates of the range of 6 to 60 mesh, pressing the detergent particles into a solid form-retaining briquetted tablet at a pressure of about 10 to 100 pounds per square inch to form a tablet which is readily disintegrable in water and applying to the tablet about .25 to 5% of a readily water soluble synthetic organic film-forming polymer consisting of polyvinyl alcohol, polyvinylpyrrolidone, sodium carboxymethyl cellulose and hydroxypropyl methyl cellulose to form on the briquette surface a water soluble film which is of strength sufficient to help make the detergent tablet resistant to abrasion and solubility in water. When dry, and of solubility such that the detergent tablet is readily disintegrable in water.

2. A process for making a briquetted detergent tablet which is resistant to abrasion and accidental breakage, when dry, and readily disintegrable in water, comprising mixing together 4 to 14% of a water soluble nonionic synthetic organic detergent which is an alkyl phenox ypolyoxyethylene alcohol having 6 to 14 carbon atoms in the alkyl group and 4 to 12 ethylene oxide units, 1 to 5% of a water soluble metal salt of higher alkyl benzene sulfonic acid in which the alkyl group is of 10 to 18 carbon atoms, 0.5 to 5% of a foam stabilizer which is a long chain fatty alcohol having 6 to 12 carbon atoms, and 30 to 75% of a water soluble inorganic alkali metal builder salt, producing therefrom a particu larly detergent containing 2 to 18% moisture, applying 15 to 50% of an aqueous solution of 25 to 46% solids content sodium silicate of Na₂O/SiO₂ ratio of 1:2 to 1:3 to the powder detergent to coat the particles with 3 to 15% sodium silicate, to cause agglomeration into larger particles and to increase the moisture content thereof to about 17 to 24%, applying to the coated detergent particles 1 to 5% of finely divided talc to form a coating on the particles, held to them by the sodium silicate, and to arrest agglomeration of the detergent particles and produce agglomerates within the range of 6 to 60 mesh, pressing the detergent particles into a solid form-retaining briquetted tablet at a pressure of 10 to 100 pounds per square inch, low enough to form a tablet which is readily disintegrable, and applying to the tablet about .25 to 5% of a readily water soluble polyvinyl alcohol, sodium silicate of Na₂O/SiO₂ ratio of about 1:2.35 to coat the particles with 6.5 to 8.5% sodium silicate, to increase the moisture content thereof to 17.5 to 20.5% and to cause agglomeration into larger particles, after about one to five minutes, applying to the coated detergent particles 1.5 to 2.5% of finely divided talc to form a coating on the tablet held to them by the sodium silicate, and to arrest agglomeration of the detergent particles and produce agglomerates within the range of 6 to 60 mesh, pressing the detergent particles into a solid form-retaining tablet at a pressure of 40 to 90 pounds per square inch, low enough to form a tablet which is readily disintegrable in water, spraying the tablet with 0.3 to 1.0% readily water soluble polyvinyl alcohol, in aqueous solution, the polyvinyl alcohol being of a weight average degree of polymerization of about 30 to 300 and a polyvinyl acetate content of about 10 to 30% thereof, and drying the polyvinyl alcohol solution to form a water soluble protective film coating.

4. A water soluble detergent briquette which is resistant to abrasion and accidental breakage, when dry, and disintegrates readily in water, comprising a multiplicity of solid particles composed of a homogeneous mixture of about 4 to 14% of a water soluble nonionic organic poly ethoxy detergent selected from the group consisting of ethoxylated alkyl phenol, ethoxylated higher fatty alcohol, ethoxylated higher fatty acid and ethoxylated propylene oxide polymers and about 30 to 75% of a water soluble inorganic alkali metal builder salt of 16 to 25% moisture content, in the form of adhering particles initially of moisture content up to 21%, consecutively coated with 3 to 20% water soluble alkali metal silicate and 0.5 to 5% of finely divided water insoluble silicate, the coated particles substantially all within the size range of 6 to 60 mesh being lightly compacted at a pressure of about 10 to 100 pounds per square inch to form a shaped briquette, which is coated with an adhering and binding film of 0.25 to 5% of a readily water soluble polyvinyl alcohol of a weight average degree of polymerization of about 30 to 300 and a polyvinyl acetate content of about 10 to 30% which forms on the surface of the detergent briquette a water soluble coating of an average thickness from about 0.1 to 0.8 millimeter.

5. A water soluble detergent briquette which is resistant to abrasion and accidental breakage, when dry, and disintegrates and dissolves readily in water, comprising a multiplicity of agglomerated spray dried solid particles of diameters substantially within the range of 0.25 millimeter to 4 millimeters, composed of homogeneous particles comprising a mixture of 7 to 12% of nonyl phenox ypolyoxyethylene alcohol of about 9 to 15 ethoxy groups, 1.5 to 5% of sodium alkyl benzene sulfonate detergent in which the alkyl group is of 12 to 15 carbon atoms, 0.5 to 3% of fatty alcohol of 12 to 18 carbon atoms and 30 to 50% of sodium tripolyphosphate coated with 6.5 to 8.5% of sodium silicate of Na₂O/SiO₂ ratio of about 1:2.35 and, over the silicate coating a coating of 1.5 to 2.5% talc, the coated particles being in the form of adhering particles of moisture content of 17.5 to 20.5%, lightly compacted at a pressure of about 10 to 100 pounds per square inch, the compacted tablet being coated with an adhering and strengthening binding film of 0.3 to 1.0% of a readily soluble polyvinyl alcohol of a weight average degree of polymerization of about 30 to 300 and a polyvinyl acetate content of 15 to 25% which forms on the surface of substantially the whole detergent briquette a water soluble coating of thickness averaging about 0.02 to 0.1 millimeter.

References Cited by the Examiner

UNITED STATES PATENTS
3,232,165 8/1945 MacMahan ——— 332—135 XR
2,636,008 4/1953 Jurgensen et al. ——— 292—93
2,855,367 10/1958 Buck ——— 252—138
2,875,155 2/1959 Miles ——— 252—138
FOREIGN PATENTS
141,503 6/1951 Australia.

OTHER REFERENCES

JULIUS GREENWALD, Primary Examiner.