STABILIZED OPAQUE DETERGENT COMPOSITION

Douglas Woodruff, Maresgo, Ill., assignor to Morton International, Inc., a corporation of Delaware


3 Claims. (Cl. 252—89)

This invention is a division of my application Ser. No. 329,873, filed Dec. 11, 1963, now Patent No. 3,340,217 and relates to the production of novel cross-linked polymeric latices of the type useful in opacifying aqueous liquid detergent compositions, to opacified detergent compositions made therefrom, and to the process of opacifying aqueous liquid detergent compositions.

An aqueous liquid detergent composition, as the term is used herein, is one containing water, a surface active agent and optionally one or more of the following ingredients: a foam stabilizer, a foam booster, a small amount of a hydrotrope, e.g. an alcohol. Usually the whole composition is adjusted to a neutral pH. The above type composition is often characterized as a light-duty liquid detergent. A so-called general-purpose or a heavy-duty liquid detergent may contain, in addition, one or more of the so-called alkaline boosters, such as alkali metal silicates, carbonates, polyphosphates and the like.

Aqueous liquid detergents are used extensively in dish washing, laundering, bathing, and in general purpose cleaning preparations. They frequently contain solubilizing aids (hydrotropes) such as sodium benzene sulfonate, sodium toluene sulfonate, sodium xylene sulfonate and/or alcohol. They are usually clear in appearance and have varying degrees of viscosity.

Dyes and particularly opacifying agents are conventionally added to these products to improve their attractiveness to consumers, who, through long exposure to cosmetic products in the form of creams and lotions, have come to associate a creamy or opague, milky appearance with mildness, softness and luxuriousness.

Polymer latices of varying descriptions have heretofore been used to opacify detergent formulations. However, many liquid detergents which are opacified with conventional polymer latices, particularly those containing alcohols, display poor storage stability and often soon deposit a sludge-like material which destroys the attractiveness of the product and thereby defeats the original objective.

It would, therefore, be desirable to provide improved polymer latices which have utility in the production of stable, opacified liquid detergent compositions.

Accordingly, one object of this invention is the provision of polymer latices for use in opacifying liquid detergent compositions.

Another object of this invention is the provision of a novel improved process for producing improved opacifier latices.

A further object is the provision of stable, opacified liquid detergents containing various concentrations of alcohol.

Another object of this invention is the provision of polymer latices which are useful in opacifying liquid detergent compositions containing a hydrotrope.

Still another object is the provision of polymer latices for use in opacifying commercial cleaning and bleaching preparations such as toilet bowl cleaners, liquid laundry bleaches and household ammonia.

A still further object of this invention is the provision of a process for opacifying liquid detergent compositions.

The fulfillment of these and other objects of the present invention may be better understood by reference to the following specification and appended claims.

Accordingly, in one broad form, the present invention comprises an interpolymer latex, said interpolymer containing in cross-linked polymerized form a proportion of a monomer selected from the group consisting of styrene and methylated styrene and a minor proportion of an unsaturated acid, a hydrophilic monomer and up to 2 parts of divinyl benzene per 100 parts of total monomer. More particularly the interpolymer comprises from about 78 to 96 parts by weight of a monomer selected from the group of styrene and methylated styrenes, from about 1 to 20 parts by weight of an unsaturated acid selected from the group of methacrylic acid, acrylic acid and itaconic acid, and from 1 to 20 parts by weight of a hydrophilic monomer selected from the group consisting of glycidyl methacrylate, and glycidyl acrylate, and up to about 2 parts by weight of divinyl benzene, the proportions of said monomers being selected to total 100 parts.

Another broad form of the present invention is a process for producing the herein above described cross-linked interpolymer latex which preferably comprises carrying out said polymerization by dividing said monomers into two fractions wherein the first contains a major proportion of the monomer of the group consisting of styrene and methylated styrene, a major proportion of the unsaturated acid monomer and all of the divinyl benzene monomer, said first fraction being added as a first monomer phase to an aqueous polymerization medium containing a surface active agent and a free radical catalyst and upon completion of the addition of the said first monomer fraction, adding a second monomer fraction, containing the hydrophilic monomer and the remaining portion of monomers.

The interpolymer latex product preferably has a solids content of from about 30 to 50 percent by weight on a total latex basis.

Another form of the present invention is a stable opacified aqueous liquid detergent composition containing a detergent selected from the group consisting of anionic and nonionic surface active agents and an opacifying latex as above defined. Of particular interest are detergent compositions which contain alcohols as solubilizing aids and/or hydrotropes. The term detergent or surface active agent also includes specific surface active agents which are known to the art as foam boosters and/or foam stabilizers for their particular function in the detergent formulation. Preferably the opacifier is present (on a solids basis) in amounts of from 0.2 to 14 parts per 100 parts of surface active agent. The alcohol is preferably present in amounts of from 3.6 to 83 parts per 100 parts of the same basis, and when present the hydrotrope, other than alcohol, preferably in amounts of from 1.8 to 83 parts.
Expressed as percentages, one specific group of detergent formulations may contain the following:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent (by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface active agent</td>
<td>18-55</td>
</tr>
<tr>
<td>Alcohol</td>
<td>2-15</td>
</tr>
<tr>
<td>Hydro trope</td>
<td>1-10</td>
</tr>
<tr>
<td>Water</td>
<td>60-80</td>
</tr>
<tr>
<td>Opacifier latex-solids (30-50% solids)</td>
<td>1-5</td>
</tr>
</tbody>
</table>

Anionic and nonionic surface active agents utilized in the opacified liquid detergents of the present invention include sodium dodecylbenzene sulfonate, alkali salts of complex organic phosphate esters, alkyl aryl sulfonates, sodium lauryl ether sulfates, sodium lauryl sulfate, the octyl nonyl phenoxy (polyethylenoxy)ethanols, polyoxyalkylene ethers, polyoxyethylene sorbitan fatty acids and fatty acid alkanolamides, and the like.

Although, as previously pointed out, the latexes herein described are particularly useful in opacifying liquid detergents containing alcohol, it should be noted that they are also effective in opacifying light duty liquid detergents, heavy duty liquid detergents, shampoos, hair-waving solutions, liquid toilet bowl cleaners, laundry bleaching liquids and household ammonia, which compositions contain materials which adversely affect the stability of ordinary opacifying latexes.

In the interpolymer latex compositions of the present invention the monomers may be present in varying amounts. In the preferred aspects of this invention, monomers of the group of styrene and methylated styrene are present in amounts of from about 85 to 95 parts by weight per 100 parts of total monomer and most preferably from 87 to 93 parts by weight on the same basis.

Of the aforesaid monomers, styrene is preferred. Exemplary of the methylated styrene monomers useful in preparing the interpolymer latexes of the present invention are mononitrile styrenes, such as 4-methyl styrene, and dimethyl styrenes, such as 2,4-dimethyl styrene. It should be understood that mixtures of styrene and/or methylated styrenes can also be used.

The unsaturated monomeric acids such as methacrylic acid, acrylic acid and itaconic acid may be used interchangeably in preparing the interpolymer latex compositions of the present invention. In addition to forming an essential component of the interpolymer latexes of this invention, the unsaturated acids also function to impart freeze-thaw and mechanical stability to the resultant latex. In the most preferred embodiment of the present invention they are used in proportions of from 1 to 10 parts by weight on a 100 parts of total monomer basis.

Glycidyl methacrylate or glycidyl acrylate is a hydrophilic monomer which is essential to the successful operability of the latexes of the present invention, and each may be used interchangeably in the polymerization process. It is preferred to use from 2 to 10 parts by weight on a 100 part of total monomer basis.

Divinylbenzene is a cross-linking agent which is in the proportions used imparts stability to the resultant latex.

The cross-linked character of the latexes of the present invention is attested to by the fact that upon drying at room temperature, there is obtained a particulate solid which is insoluble in acetone, methyl ethyl ketone, toluene, dimethylformamide and benzene. The latexes of the present invention are non-film forming, and preferably have an average particle size of less than 0.5 micron. The amount of divinylbenzene used is critical and should not exceed approximately 2 parts by weight per 100 parts of total monomers. In the present compositions, divinylbenzene in excess of about 2 parts by weight tends to reverse the stability which lesser amounts impart and induces coagulation of the latex. The divinylbenzene used herein is a technical grade in the form of a 55 percent active solution containing 45 percent of ethyl vinylbenzene. Ethyl vinylbenzene has of course no functional capability of cross-linking.

The latices of the present invention are further characterized by their unusual stability to coagulation or precipitation by methanol, the usual polymer emulsion precipitating agent, or by dilute aqueous solutions of hydrochloric acid. It is believed that this stability is the result of a combination of attributes such as the cross-linked condition of the copolymers comprising the latices, coupled with the effect of the hydrophilic monomers, glycidyl methacrylate or glycidyl acrylate.

Exemplary of the alkaline materials which are satisfactory in the pH adjustment of the present latices are the following: Monoethanolamine, diethanolamime, triethanolamine, ammonium hydroxide, sodium hydroxide, monosopropylammonium, diisopropanolamine, trisopropylamine, 3-aminopropyl, morpholine and tetra-ethanol ammonium hydroxide. These alkaline materials are used to adjust the pH of the latex product to from about 7 to 11.

The type of surface active agents used in the polymerization procedure of the process of the present invention is not critical. Anionic surfactants, exemplified by alkyl aryl sulfonates and/or alkyl sulfates, may be used alone or in the blends with nonionic surfactants, in amounts ranging from about 1 to 10 percent on a total monomer basis.

The time of polymerization is likewise not critical and it should be understood that by utilizing certain catalyst systems, such as, for example, redox systems, the polymerization may be carried out in a relatively short time. Accordingly, the time of polymerization may extend from about 15 to about 240 minutes, although for most purposes from about 30 to 180 minutes are adequate.

The polymerization procedure of the present invention employed to prepare the herein described latexes is an aqueous emulsion polymerization technique utilizing free radical or peroxide type catalysts. It is possible to prepare the present opacifier latexes by either one or a two phase monomer addition procedure. However, a two phase monomer addition procedure is preferred, as it results in a latex which imparts greater storage stability to the liquid detergent in which it is incorporated than that produced by a one monomer phase addition.

In the most preferred process of the present invention, a two phase monomer addition procedure is employed in which from 60 to 90 percent by weight of the total styrene or methylated styrene used, from 50 to 90 percent by weight of the total unsaturated acid used, and 100 percent by weight of the total divinylbenzene used are added as a first monomer phase or fraction or a reaction vessel containing water, a surface active agent, and a free radical catalyst. Upon completion of the addition of the first monomer phase, a second monomer fraction or phase containing the balance, i.e. from 10 to 40 percent by weight of the total styrene used, 20 to 50 percent by weight of the total unsaturated acid used, and 100 percent by weight of the total hydrophilic monomer used, is added. The temperature is maintained at from 80 to 95° C. until completion of the monomer addition. Upon completion of the reaction, the pH is adjusted to from 7 to 11 as above indicated. It should be understood that the parts by weight or percentages referred to herein have reference to monomeric constituents only and do not include diluents, carriers, additives, or other materials which may be used in conjunction with the monomers in the polymerization process.

In the preferred two-phase monomer addition procedure of the present invention, the divinylbenzene should be present in the first monomer fraction or phase which is added to the reaction vessel as a surface active agent, buffer and free radical catalyst. If divinylbenzene is added as a component of the second monomer.
phase, the resultant latex exhibits unsatisfactory stability when incorporated in a liquid detergent composition.

For a more complete understanding of the present invention, reference is now made to the following specific examples illustrating the preparation of the various copolymer latices, their evaluation as opacifiers for liquid detergent compositions containing various concentrations of alcohol, and opacified detergent compositions.

**EXAMPLE 1**

<table>
<thead>
<tr>
<th>Parts by Weight</th>
<th>Parts by Weight per 100 Parts Total Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5 parts active</td>
<td>3 Active</td>
</tr>
</tbody>
</table>

The kettle charge is added to a suitable vessel equipped with a reflux condenser, mechanical stirrer, addition funnel and thermometer.

The charge is heated to 90-92° C. with continuous stirring. When the charge reaches this temperature, the catalyst premix is added with stirring. Upon completion of the addition of the catalyst premix, monomer Phase A is added to the stirred reaction medium at a uniform rate over a period of about 60 minutes. After the addition of monomer Phase A, the addition of monomer Phase B is begun at a constant rate over a period of about 30 minutes. The entire reaction is carried out at temperatures varying between 85° C. and 95° C. Stirring and heating at this temperature is continued for about 60 minutes after the completion of the addition of monomer Phase B, after which the batch is neutralized with diethanolamine (neutralization charge) and heated at 90° C. for an additional 30 minutes and then cooled to form the finished product. The final product has a solids content of about 40%, an average particle size of less than 0.5 microns and a pH of about 9.5.

Evaluation of opacifier stability

To evaluate the stability of a typical liquid detergent opacified with the composition of Example 1, the following liquid detergent was employed in this as well as in tests hereinafter described as representative of a typical aqueous light-duty liquid detergent containing alcohol as the solubilizing aid.

<table>
<thead>
<tr>
<th>Parts by weight</th>
<th>11.0</th>
<th>5.0</th>
<th>25.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonyl phenoxypolyethylenoxy)ethanol (15 moles ethylene oxide)</td>
<td>Lauric diethanolamide</td>
<td>Sodium alkyl aryl sulfonate (57.5% active)</td>
<td>&lt;ref&gt;46&lt;/ref&gt;</td>
</tr>
</tbody>
</table>

Ethyl alcohol 8.0, Water, ion exchanged 40.5, Dilute sulfuric acid to adjust to about pH 7.0.

One part by weight of opacifier latex prepared as described in Example 1 is dispersed in 10 parts by weight of ion exchanged water. This entire latex dispersion is then added to 90 parts by weight of the above liquid detergent solution with efficient stirring. This produces a stable, opaque, milky lotion-like liquid which is tested for stability by storage at 125° F. There is no change in the appearance of the opacified detergent after more than 30 days storage at 125° F.

Example 1 was repeated except that the divinylnbenzene component was added with the second or phase B component. The resultant latex when formulated with the detergent composition described above showed deterioration and loss of stability after two days accelerated storage at 125° F.

**EXAMPLE 2**

A copolymer latex is prepared as set forth in Example 1 with the exception that vinyl toluene (4-methyl styrene) is substituted for styrene. When the resultant opacified detergent composition of Example 1 is tested for stability by storage at 125° F., there is no change in the appearance of the opacified detergent after more than 30 days storage at 125° F.

**EXAMPLE 3**

A copolymer latex is prepared as set forth in Example 1 with the exception that in monomer Phase B, 30 parts of glycidyl acrylate is substituted for 30 parts of glycidyl methacrylate. When this opacified detergent composition is tested for stability by storage at 125° F., there is no change in the appearance of the opacified detergent after more than 30 days.

**EXAMPLE 4**

A copolymer latex is prepared as in Example 1 except that acrylic acid is substituted for methacrylic acid. The opacified detergent composition of Example 1 using this latex is stable for 30 days at 125° F.

**EXAMPLE 5**

A copolymer latex is prepared as set forth in Example 1 with the exception that in monomer Phase B, 30 parts of styrene is substituted for 30 parts of glycidyl methacrylate.

When this opacified detergent composition is tested for stability by storage at 125° F., there is considerable separation in less than 24 hours, as evidenced by a sludge-like layer on the bottom of the container and a loss of opacity in the detergent.

**EXAMPLES 6 to 11**

The procedure of Example 1 is repeated in the following Examples 6, 7, 8, 9 and 10, with the only exception that substitutions for glycidyl methacrylate are made in monomer Phase B as indicated in Table I. In Example 11, the proportion of glycidyl methacrylate is increased to approximately one and one-half times its concentration in Example 1. Each latex so prepared is evaluated as an opacifier according to the procedure set forth in Example 1, with the results shown in Table I. The quantities of ingredients in Table I are expressed as parts by weight.

**TABLE 1**

<table>
<thead>
<tr>
<th>Examples</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer Phase B:</td>
<td>65</td>
<td>85</td>
<td>85</td>
<td>85</td>
<td>85</td>
<td>70</td>
</tr>
<tr>
<td>Monofunctional Acrylic Acid</td>
<td>8</td>
<td>8</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Methyl Methacrylate</td>
<td>40</td>
<td>40</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Cellophane Acrylate</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Itaconic Acid</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Divinylbenzene</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

1 Considerable separation in less than 94 hours.
2 No change in appearance after 30 days.

The results of opacifier evaluations of the latices prepared according to Examples 6 through 11 illustrate the essentiality of glycidyl methacrylate or glycidyl acrylate to the preparation of interpolymer latices which exhibit stability in opacifying aqueous liquid detergent compo-
sitions having an appreciable alcohol content. Example 11 demonstrates that increasing the glycidyl methacrylate content of the latex does not impair its opacifying capability.

**EXAMPLE 12**

An interpolymer latex is prepared as set forth in Example 1 with the exception that the addition of diethanolamine is omitted. The resultant pH is 5.7. When the detergent composition described in Example 1 is opacified using the copolymer latex of Example 12 and is tested for storage stability as before, there is a slight separation after one week. The stability of the detergent opacified with the latex of Example 12, when compared with the stability of the same detergent composition opacified with the latex of Example 1, illustrates the additional stability achieved by the regulation of the pH from 7 to 11.

**EXAMPLE 13**

An interpolymer latex is prepared as set forth in Example 1 with the exception that the addition of diethanolamine is omitted. The resultant pH is 5.7. When the detergent composition described in Example 1 is opacified using the copolymer latex of Example 12 and is tested for storage stability as before, there is a slight separation after one week. The stability of the detergent opacified with the latex of Example 12, when compared with the stability of the same detergent composition opacified with the latex of Example 1, illustrates the additional stability achieved by the regulation of the pH from 7 to 11.

**EXAMPLE 14**

The procedure followed in the preparation of the latex of Example 13 is that set forth in Example 1. The resultant opacified detergent containing 1% by weight of the latex of Example 13 is stable for more than 30 days upon storage at 125°F.

**EXAMPLE 15**

The procedure followed is the same as that of Example 1 with the exception that the monomer phase is added as a single charge rather than the two step addition of Example 1. The evaluation of the latex of Example 14 as an opacifier was carried out in the same manner as that of Example 1. The resultant opacified latex is stable at 125°F for two weeks.

**EXAMPLE 16**

Opacified liquid detergent composition

An opacified liquid detergent is prepared utilizing the copolymer latex obtained in Example 1. The ingredients listed below are dispersed in water to form a homogeneous aqueous dispersion:

1. Copolymer latex 40% solids (Example 1) — 1
2. Isopropyl alcohol — 5
3. Ammonium salt of sulfate ester of an alklyphenoxypoly(ethyleneoxy)ethanol (55% minimum activity) (Alipol CO-436) — 20
4. Lauric diethanolamide (Superamide L-9) — 3
5. Alkyl aryl sulfonate (57.5% active) (Ultrawet 60-K) — 25
6. Water — 46
7. Acid (dilute sulfuric) to pH 6.5 to 7.5.

This results in a milky, lotion-like detergent composition which exhibits excellent storage stability.

**EXAMPLE 18**

Opacified liquid detergent composition

The procedure followed is the same as that of Example 1 with the exception that the monomer phase is added as a single charge rather than the two step addition of Example 1. The evaluation of the latex of Example 14 as an opacifier was carried out in the same manner as that of Example 1. The resultant opacified latex is stable at 125°F for two weeks.

**EXAMPLE 19**

This example illustrates the results obtained when the amount of divinylbenzene exceeds two parts per 100 parts of total monomer.
EXAMPLE 19

Ten milliliters of each of the latices prepared in accordance with Examples 1 and 13 are added to approximately 100 milliliters of methanol with thorough mixing. The resultant mixture in each instance is homogeneous and free from evidence of coagulation or precipitation. The addition of an aqueous solution of hydrochloric acid containing approximately 10% by weight of HCl fails to induce coagulation in either of the above latices.

EXAMPLE 20

Each of the latices prepared in accordance with Examples 1 and 13 is allowed to evaporate at approximately 70° F. to obtain the nonvolatile matter of each. Each latex yields a powdery particulate solid which exhibits no film-forming tendencies and which is insoluble in acetone, ethyl methyl ketone, benzene, toluene and dimethylformamide.

From the foregoing examples, it may be seen that the novel copolymers of the present invention result in latices which are particularly useful in opacifying liquid detergents. Examples 1 through 11 demonstrate the criticality of the monomers glycidyl methacrylate and glycidyl acrylate in the compositions herein described to provide an opacified detergent solution displaying storage stability. Example 12 illustrates the optimum pH range of the finished latex. Example 13 illustrates the use of a quantity of glycidyl methacrylate which is substantially less than that used in Example 1.

Example 14 illustrates that it is possible to prepare the latices of the present invention by a single monomer admixture addition rather than a two phase technique. However, it will be observed that the resultant opacified liquid detergent employing such latex lacks that degree of stability which the same liquid detergent opacified with the latex of Example 1 displays. This lends weight to the premise that a two-step addition procedure produces a latex which has enhanced opacifying properties.

Example 15 demonstrates the criticality of the ratio of divinylbenzene employed. The composition of Example 1, containing 1.3 percent by weight on a monomer basis of divinylbenzene, is a stable and effective opacifier latex, whereas the composition of Example 15, containing 2.1 weight percent of divinylbenzene results in a coagulated, useless mass.

Examples 16, 17 and 18 demonstrate various liquid detergent compositions which may be opacified by means of the present latices.

Example 19 underscores the unique stability of the present latices which are unaffected by the presence of large volumes of methanol, a solvent generally employed as a coagulating agent for aqueous polymer latices. Example 20 illustrates the non-film forming, cross-linked characteristics of the interpolymers of the present invention.

While several particular embodiments of this invention are shown above, it will be understood, of course, that the invention is not to be limited thereto, since many modifications may be made, and it is contemplated, therefore, by the appended claims, to cover any such modifications as fall within the true spirit and scope of this invention.

I claim:
1. A stabilized aqueous liquid opacified detergent composition consisting essentially of a surface active agent selected from the group consisting of anionic detergents, nonionic detergents and blends thereof and a cross-linked interpolymer latex, said latex being present in an amount of from 0.2 to 14 parts of polymer solids per 100 parts by weight of surface active agent, said latex comprising an interpolymer in cross-linked polymerized form containing from 78 to 96 parts by weight of a monomer selected from the group consisting of styrene and methacrylate, from 1 to 20 parts by weight of an unsaturated acid selected from the group consisting of methacryloyl, acryl, acrylic acid and fumaric acid, from 1 to 20 parts by weight of a monomer selected from the group consisting of glycidyl methacrylate and glycidyl acrylate and divinylbenzene in an amount of up to about 2 parts per 100 of total monomer, the proportions of said monomers being such as to total 100 parts in the aggregate.
2. A detergent composition according to claim 1 having from 3.6 to 83 parts of a lower alkanol per 100 parts of the surface active agent.
3. A detergent composition according to claim 1 wherein the interpolymer latex contains from 85 to 95 parts styrene, from 1 to 10 parts of methacryloyl acid, from 1 to 10 parts of glycidyl methacrylate and up to 2 parts of divinylbenzene.

References Cited

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Date</th>
<th>Inventor(s)</th>
<th>Class</th>
<th>Claims</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,060,124</td>
<td>10/1962</td>
<td>Ginn</td>
<td>252—89</td>
<td></td>
</tr>
<tr>
<td>3,156,655</td>
<td>11/1964</td>
<td>Bright</td>
<td>252—89</td>
<td></td>
</tr>
<tr>
<td>3,235,568</td>
<td>2/1966</td>
<td>TuveI</td>
<td>252—89</td>
<td></td>
</tr>
<tr>
<td>3,282,852</td>
<td>11/1966</td>
<td>Trusler et al.</td>
<td>252—89</td>
<td></td>
</tr>
</tbody>
</table>

LEON D. ROSDOL, Primary Examiner.
W. E. SCHULZ, Assistant Examiner.