PROCESS OF PREPARING AQUEOUS DISPERSION OF AN ACRYLONITRILE INTERPOLYMER AND A THERMOSETTING RESIN AND PRODUCT OBTAINED

<table>
<thead>
<tr>
<th>Dec. 30, 1958</th>
<th>P. F. SANDERS</th>
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<tr>
<td>2,866,763</td>
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<td>Filed April 16, 1956</td>
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</table>

DEIONIZED OR DISTILLED WATER

SODIUM META BISULFITE
SODIUM LAURYL SULFATE

A. ACRYLONITRILE
B. METHACRYLIC ACID
C. BUTYL ACRYLATE

ION EXCHANGE RESIN COLUMN

WEIGHT TANK AND HOMOGENIZING PREMIXER

FIRST STAGE AMMONIACAL NEUTRALIZATION TO pH VALUE 5.5 TO 6.5

POTASSIUM PERSULFATE
SODIUM LAURYL SULFATE

SECOND STAGE AMMONIACAL NEUTRALIZATION TO pH VALUE UP TO 8.0

DEIONIZED OR DISTILLED WATER

WATER-DILUTABLE, HEAT-REACTIVE PHENOL/FORMALDEHYDE RESIN

AQUEOUS AMMONIA

SINGLE STAGE AMMONIACAL NEUTRALIZATION TO pH VALUE 5.5 TO 8.0

POLYMERIZATION REACTOR

FILTER

AMMONIACAL NEUTRALIZING HEAT TREATING MIXER

FILTER

FINAL PRODUCT STORAGE INVENTOR

PHILIP F. SANDERS

BY Charles E. Bartek
AGENT
PROCESS OF PREPARING AQUEOUS DISPERSION OF AN ACRYLONITRILE INTERPOLYMER AND A THERMOSETTING RESIN AND PRODUCT OBTAINED

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Application April 16, 1956, Serial No. 578,405

14 Claims. (Cl. 260—29.3)

This invention relates to aqueous dispersion interpolymer compositions. More particularly the invention relates to stabilized aqueous dispersion compositions comprising admixtures of salts of certain acrylic acrylonitrile interpolymer characterized by resistance-stability and resistance to gelation and to a method of preparing these ammoniacal aqueous dispersions.

In copending United States patent applications Sanders Serial No. 369,890 and Sanders Serial No. 369,969, both filed July 23, 1953, now U. S. Patent No. 2,787,603, are described useful acid interpolymer prepared from a monomer mixture consisting of acrylonitrile, an alpha olefinic monocarboxylic acid selected from the group consisting of acrylic acid, methacrylic acid, ethacrylc acid, phenyl acryic acid and crotonic acid, and an ester of at least one of these acids with a saturated aliphatic mono- hydrolic alcohol having from 1 to 8 carbon atoms; and useful coating and impregnating compositions comprising such acid interpolymer.

For many coating purposes, it was found desirable to modify the acid interpolymer in the form of an aqueous dispersion with a water-dilutable, heat-reactive phenol/formaldehyde resin. In applying these aqueous dispersion compositions to metal substrates, such as in the case of wire-coating, best results ordinarily are obtained when the coating composition at the time of use is adjusted to a pH value in the range of about 9.0 to 10.0 with ammonium hydroxide or a volatile amine.

Although these aforementioned aqueous dispersions of acid interpolymer, either in the acidic state or ammoniacally adjusted to the indicated high pH value, can be satisfactorily applied to a wide variety of substrates to provide useful coated or impregnated articles, these dispersions have certain undesirable deficiencies pertinent to packaging and storage. The acidic dispersions ordinarily cannot be packaged in conventional metal containers and must be stored in glass or in metal containers interiorly protected with a coating inert toward the aqueous dispersion in order to prevent contamination with corrosion products. Even when packaged in an appropriate container, the acidic dispersions are not as storage-stable as is ordinarily desired for sale. These acidic dispersions develop coagulum and fine acid-filled polymer grit during storage, particularly when mechanical shearing conditions, such as pumping and high speed agitation, is involved in handling the material. Another deficiency of these acidic dispersions is that they are at a viscosity lower than that ordinarily desired for most uses.

The ammoniacally adjusted dispersions can be stored and subjected to pumping and agitation without development of coagulum or polymer grit, but these dispersions are lacking in viscosity-stability and resistance to gelation. The rate of viscosity-increase of these dispersions is so rapid that the material stored for a period as short as several weeks is either gelled or at a viscosity too high for application by ordinary means.

The primary object of this invention is to overcome the described deficiencies of the aqueous dispersions of the aforementioned interpolymer. An important object of this invention is to provide improved aqueous dispersion interpolymer compositions of the aforementioned class of interpolymer characterized by superior viscosity-stability, package-stability and resistance to gelation. Another object is to provide an aqueous dispersion interpolymer composition of the described class stably advanced in viscosity. A further object is to provide a method of preparing ammoniacal aqueous dispersion interpolymer compositions of a monomer mixture consisting of acrylonitrile, an alpha olefinic monocarboxylic acid selected from the group consisting of acrylic acid, methacrylic acid, ethacrylc acid, phenyl acryic acid and crotonic acid, and an ester of at least one of these acids with a saturated aliphatic monohydric alcohol whereby the resulting aqueous dispersion is characterized by viscosity-stability, package-stability and resistance to gelation. Other important objects will become apparent as the description of the invention proceeds.

These and other important objects are accomplished by preparing an aqueous dispersion of an ammonium salt of an acid interpolymer by initially preparing the acid interpolymer by emulsion polymerization in water of a mixture of polymerizable monomers consisting of (A) 30% to 80% by weight of acrylonitrile, (B) 1.5% to 15% by weight of at least one alpha-olefinic monocarboxylic acid selected from the group consisting of acrylic acid, methacrylic acid, ethacrylc acid, phenyl acryic acid and crotonic acid, and (C) 15% to 65% by weight of at least one of an acid of (B) with a saturated aliphatic monohydric alcohol having from 1 to 12 carbon atoms, forming an ammonium salt of the interpolymer by neutralizing the resulting aqueous dispersion of the acid interpolymer at a temperature in the range of about 45° C. to 95° C. with ammonium hydroxide, or in an amount sufficient to neutralize at least 10% by weight of the acid (B) component of the interpolymer and provide the aqueous dispersion with a pH value in the range of 5.5 to 6.0, and cooling the ammoniacal dispersion to a temperature below about 30° C. An advance in viscosity which is stable is imparted to the ammoniacal aqueous dispersion by maintaining it within the indicated temperature range for a period ranging from 5 minutes to about 4 hours prior to cooling. When these aqueous dispersion compositions are further modified with a heat-reactive aldehyde condensation resin, the above described invention process includes the additional step of blending a water-dilutable, heat-reactive aldehyde condensation resin selected from the group consisting of phenol/formaldehyde resin, urea/formaldehyde resin, melamine/formaldehyde resin, urea/melamine/formaldehyde resin and mixtures thereof with the aqueous dispersion of the interpolymer in either its acid-form or its ammonium salt-form, either prior to the heat-effected ammoniacal reaction or with the ammoniacal aqueous dispersion interpolymer composition subsequent to the heat-effected neutralization.

The drawing is a flow sheet of a preferred embodiment of the process of the invention.

The following specific examples represent the best modes contemplated for carrying out the invention which are given by way of illustration and not limitation. The parts and percentage figures are expressed on a weight basis unless stated otherwise.
2,886,763

3 EXAMPLE 1

Water, distilled........................................ 62.695
Sodium meta bisulfite................................... 0.035
Sodium lauryl sulfate, "Duponol" C.................. 1.000
Acrylonitrile monomer................................ 22.005
Methacrylic acid monomer............................... 1.800
Butyl acrylate monomer................................ 11.200
Potassium persulfate solution, 5.0% by wt. in distilled water......................... 2.080

---

100.000

The sodium meta bisulfite (Na₃S₂O₅) had an assay of 97.5% and a corresponding content of at least 65.58% SO₃.

The sodium lauryl sulfate was the commercial available "Duponol" C having an assay of at least 90%, the remainder being 1.5% to 3.5% of unsulfated fatty alcohol and not more than 8% of a mixture of sodium chloride and sodium sulfate.

The potassium persulfate (K₂S₂O₅) had an assay of at least 94% and a corresponding content of at least 70% S₂O₅. The acrylonitrile monomer as purchased contained 250 to 300 parts per million of organic amines as a polymerization inhibitor. These amines inhibitors were removed by passing the inhibited acrylonitrile through a column of "Amberlite" IR-120 ion exchange resin in its acid form.

The methacrylic acid monomer was the commercially available glacial grade which contained hydroquinone at a concentration of about 1000 parts per million as an inhibitor. This monomer was used without removal of the inhibitor.

The butyl acrylate monomer as purchased contained hydroquinone at a concentration of about 100 parts per million as an inhibitor. This monomer was also used without removal of the inhibitor.

In the preparation of the interpolymer dispersion, all the indicated components except the potassium persulfate solution were charged into a high speed homogenizing mixer, emulsified for about 6 minutes and transferred to a reactor equipped with means for controlled temperature variation and means for agitation. The emulsified charge was heated to 60°C while it was adequately agitated with an agitator rotating at about 200 R. P. M. When the charge reached 60°C, the potassium persulfate solution, freshly prepared by dissolving the salt in water at about 45°C, was added to the preheated charge. The initiated polymerization reaction was exothermic and heat was withdrawn from the reaction mixture in order to hold the temperature at about 60°C. Polymerization was continued until the exothermic reaction was no longer detectable; about 143 minutes after the addition of the persulfate. The product was held at a temperature of 60°C for 90 minutes additional and cooled to room temperature. Analysis of product samples taken at this stage showed a non-volatile content of 34.5% by weight, indicating that the monomer conversion was at least 98.5%.

The resulting aqueous dispersion of the acidic interpolymer had a pH value of 3.8 and was characterized by an average particle size of .22 micron. The interpolymer separated from the aqueous dispersion was characterized by a relative viscosity of 6.6 as determined with an A. E. T. M. #200 Ostwald-Cannon-Fenske viscometer at 25°C using dimethyl formamide as the solvent for preparing the viscosity test solution at 0.5% by weight of the interpolymer.

This stabilized aqueous dispersion interpolymer product of Example 1 was filtered through felt and divided into aliquot portions which were treated respectively as follows with the final composition in each instance adjusted with distilled water to a non-volatile content of 30% by weight.

**Sample A.** Diluted with distilled water without any other treatment.

**Sample B.** The aqueous dispersion product neutralized to a pH value of 9.0 with ammonium hydroxide and diluted.

**Sample C.** Diluted with distilled water, heated to 75°C in about 5 minutes, held at this temperature for 15 minutes and immediately cooled to room temperature.

**Sample D.** Ammonia neutralized to a pH value of 7.5, heat treated at 75°C as described for sample C and immediately cooled.

**Sample E.** Treated as described for sample D except that the ammoniacal neutralization was to a pH value of 9.0.

**Sample F.** Heat-treated as described for sample C and thereafter ammoniacally neutralized to a pH value of 9.0.

**Sample G.** Initially neutralized to a pH value of 7.5 with ammonium hydroxide, heat-treated as described for sample D and thereafter ammoniacally neutralized to a pH value of 9.0.

The viscosity of these respective samples was determined at 25°C using a Brookfield viscometer operating at 6 R. P. M. with a #2 spindle. The samples were then stored in an oven at 50°C, periodically removed from the storage oven, cooled to 25°C, and measured for viscosity to determine the effect of storage at 50°C on viscosity stability. When the viscosity increased beyond the practical range of the #2 spindle, other standard spindles were used with the Brookfield viscometer.

The viscosity data for these samples recorded in centipoises are shown in Table 1.

<table>
<thead>
<tr>
<th>Viscosity</th>
<th>Sample A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>20</td>
<td>100</td>
<td>20</td>
<td>129</td>
<td>9,020</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>42 days</td>
<td>20</td>
<td>15,000</td>
<td>20</td>
<td>60</td>
<td>9,200</td>
<td>100</td>
<td>70</td>
</tr>
<tr>
<td>42 days</td>
<td>20</td>
<td>38,000</td>
<td>20</td>
<td>60</td>
<td>10,000</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>80 days</td>
<td>20</td>
<td>55,000</td>
<td>20</td>
<td>60</td>
<td>9,020</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>161 days</td>
<td>15,000</td>
<td>90</td>
<td>15,000</td>
<td>90</td>
<td>9,020</td>
<td>15,000</td>
<td>15,000</td>
</tr>
</tbody>
</table>

The data in Table 1 show that sample D, representing ammoniacal neutralization of the acidic dispersion product to a pH value of 7.5 followed by heat-treatment was outstandingly stable in viscosity. This sample did not gel or significantly increase in viscosity during one year of storage. This sample remained package-stable and free of coagulation and formation of fine grit polymer. While the data for samples A and C show moderate viscosity stability for the aqueous dispersion interpolymer composition in its unneutralized state, these samples were not package-stable and heating did not provide an advance in the initial viscosity. The aged samples showed coagulation and development of fine grit polymer.

Sample B exhibited a desirable initial viscosity, but the product was unstable in viscosity and bodied during 28 days of storage to a viscosity impractical for use. Sample E, equivalent to sample B but heat-treated, was advanced to a high initial viscosity impractical for use and gelled more rapidly than sample B.

Data for samples F and G show that when the alkalinity of the heat-treated aqueous dispersion interpolymer composition in either its acidic form or ammonium

---

Table 1

EFFECT OF STORAGE AT 50°C ON VISCOSITY STABILITY

The viscosity of these respective samples was determined at 25°C using a Brookfield viscometer operating at 6 R. P. M. with a #2 spindle. The samples were then stored in an oven at 50°C, periodically removed from the storage oven, cooled to 25°C, and measured for viscosity to determine the effect of storage at 50°C on viscosity stability. When the viscosity increased beyond the practical range of the #2 spindle, other standard spindles were used with the Brookfield viscometer.

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<th>C</th>
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<th>F</th>
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<td>Initial</td>
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<td>129</td>
<td>9,020</td>
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<tr>
<td>42 days</td>
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<td>15,000</td>
<td>20</td>
<td>60</td>
<td>9,200</td>
<td>100</td>
<td>70</td>
</tr>
<tr>
<td>42 days</td>
<td>20</td>
<td>38,000</td>
<td>20</td>
<td>60</td>
<td>10,000</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>80 days</td>
<td>20</td>
<td>55,000</td>
<td>20</td>
<td>60</td>
<td>9,020</td>
<td>140</td>
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<tr>
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<td>15,000</td>
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Sample B exhibited a desirable initial viscosity, but the product was unstable in viscosity and bodied during 28 days of storage to a viscosity impractical for use. Sample E, equivalent to sample B but heat-treated, was advanced to a high initial viscosity impractical for use and gelled more rapidly than sample B.

Data for samples F and G show that when the alkalinity of the heat-treated aqueous dispersion interpolymer composition in either its acidic form or ammonium
The data in Table 2 show that samples H, J, K and L are resistant to gelation for a period of at least 164 days at 50° C. Of these, sample L was lacking in package stability because of continued coagulation and growth of polymer grit during storage. Samples which were adjusted to a pH value of 9.0 rapidly increased in viscosity during storage and gelled within the 164 days' test period.

The data show that the phenolic resin can be blended with the aqueous dispersion interpolymer composition either before or after the heat-effected ammoniacal reaction without altering the stability of the product. A comparison of the data for samples H and J show that the heat-reactive phenol/formaldehyde resin is advantageously blended with the aqueous dispersion interpolymer composition prior to the ammoniacal neutralization when it is desirable to provide the composition with an advanced viscosity which is stable.

EXAMPLE 2

Unstabilized aqueous dispersion interpolymer composition, 41% by wt.

| Water-dilutable, heat-reactive phenol/formaldehyde resin, BR-15100, 66% by weight | 4,85 |
| Ammonium hydroxide, 29% NH₃ | 7.6 |
| Distilled water | 24.05 |

100.00

The unstabilized aqueous dispersion interpolymer composition was prepared as described in Example 1 using the same relative proportions of the respective monomers, that is, acrylonitrile 63%, butyl acrylate 32% and methacrylic acid 5%. The polymerizable mixture consisted of the following composition:

| Parts by wt. |  |
| Acrylonitrile monomer | 26.10 |
| Butyl acrylate monomer | 13.35 |
| Methacrylic acid monomer | 2.07 |
| Sodium lauryl sulfate, "Duponol" C | 0.22 |
| Sodium meta bisulphite | 0.04 |
| Potassium persulphate | 0.12 |
| Water, distilled | 58.10 |

100.00

The emulsion polymerization was carried out at 60° C. The monomer conversion was 98.8% and the aqueous dispersion product had a polymer content of 41.0%. The pH value of the aqueous dispersion was 3.7 at 25° C. and the average particle size of the interpolymer in the dispersion was .25 micron. The interpolymer had a relative viscosity of 6.3 using dimethyl formamide as the solvent. The unstabilized aqueous interpolymer dispersion was filtered through felt before it was used in the preparation of the product of Example 2.

The indicated content of ammonium hydroxide corresponds to the approximate amount added to raise the pH value of the acidic aqueous dispersion at 3.7 to an ammoniacal alkalinity of 7.65.

The component of the composition of Example 2 were blended at room temperature until uniform. The resulting mixture was heat processed as follows: (a) heated in 5 minutes to 45° C, (b) heated in another 5 minutes to 65° C, (c) heated in another 5 minutes to 85° C, and thereafter held at this latter temperature for 120 minutes. Samples were taken at 45° C, 65° C, 85° C, and at intervals while the temperature was held at 85° C. The viscosity data reported in centipoises for these samples measured at 25° C. using the Brookfield viscosimeter at 6 R. P. M. are shown in Table 3.
Table 3

**EFFECT OF HEATING TIME ON VISCOSITY ADVANCEMENT**

<table>
<thead>
<tr>
<th>Sample:</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>30</td>
</tr>
<tr>
<td>(a) After heating to 45° C. in 5 minutes</td>
<td>65</td>
</tr>
<tr>
<td>(b) After heating to 65° C. in 10 minutes</td>
<td>110</td>
</tr>
<tr>
<td>(c) After heating to 85° C. in 15 minutes</td>
<td>210</td>
</tr>
<tr>
<td>(d) Thereafter holding at 85° C. for 10 minutes</td>
<td>245</td>
</tr>
<tr>
<td>(e) Thereafter holding at 85° C. for 20 minutes</td>
<td>235</td>
</tr>
<tr>
<td>(f) Thereafter holding at 85° C. for 30 minutes</td>
<td>235</td>
</tr>
<tr>
<td>(g) Thereafter holding at 85° C. for 60 minutes</td>
<td>210</td>
</tr>
<tr>
<td>(h) Thereafter holding at 85° C. for 90 minutes</td>
<td>170</td>
</tr>
<tr>
<td>(i) Thereafter holding at 85° C. for 120 minutes</td>
<td>170</td>
</tr>
</tbody>
</table>

These data show that the ammoniacal neutralized aqueous dispersion product can be heated for a relatively short period of time to provide a desirable viscosity advancement. Prolonged heating causes the viscosity of the product to level off at a value below the maximum viscosity-advance observed.

These samples were package-stable, viscosity-stable and gelation-resistant during storage at room temperature for a period of at least one year.

**EXAMPLE 3**

Part 1:
- Water, deionized: 59.05 parts by wt.
- Sodium lauryl sulfate, "Duzon" C: 0.20 part
- Sodium metal bisulfitic: 0.03 part
- Acrylonitrile monomer: 24.20 part
- Methacrylic acid monomer: 1.92 part
- Butyl acrylate monomer: 12.30 part
- Potassium persulfate solution, 5% by wt. in distilled water: 2.30 parts
- Latex total: 100.00 parts

Part 2: Ammonium hydroxide 29% NH₃ to pH value 5.5 to 6.5: 0.15 parts

Part 3:
- Water-dilutable, heat-reactive phenol/formaldehyde resin, BR-15100, 6% by wt. in water: 6.45 parts
- Water, deionized: 21.30 parts

Part 4: Ammonium hydroxide 29% NH₃ to pH value 7.2: 1.00 part

Total enamel: 128.90 parts

The components were the same as those used in Examples 1 and 2. Part 1 representing the unstabilized aqueous dispersion interpolymer composition was prepared following the process described for the preparation of the aqueous dispersion product of Example 1, carrying out the emulsion polymerization at about 60° C. The resulting aqueous dispersion product had a pH value of 3.8, an average particle diameter of about 0.20 micron, and a polydispersity of 37.5% by weight. The polymer had a relative viscosity of 6.5 using dimethyl formamide as the solvent.

After completion of the polymerization in part 1, the resulting acidic aqueous dispersion interpolymer composition while at the temperature of about 60° C. was neutralized with the ammonium hydroxide of part 2 to a pH value in the range of 5.5 to 6.5. The added amount of ammonium hydroxide was sufficient to neutralize at least 10% by weight of the methacrylic acid component of the interpolymer. The combined parts 1 and 2 were filtered through felt, transferred to a storage tank as an intermediate product for subsequent use and allowed to cool to room temperature. In the ammoniacal neutralization stage, the combined parts 1 and 2 ordinarily are exposed to an elevated temperature in the range of 60° C. for about 30 minutes or longer. Completion of this intermediate ammoniacal monomer product consisting of combined parts 1 and 2 represents a preferred and convenient point of interruption in the commercial manufacturing process. This intermediate product is viscosity-stable and storage-stable. It is adequately low in 1% aqueous solution for convenient filtering and it can be reheated, cooled and subjected to mechanical operations, such as agitation and pumping, after filtration without introducing fine-grit formation or coagulation.

When preparation of the final product of Example 3 was resummed, part 3 was blended with the intermediate product; that is, the combined parts 1 and 2 which had been filtered and stored, combined parts 1, 2 and 3 were heated to 87° C. with agitation and part 4 was added thereto as a second stage ammoniacal neutralization to adjust the composition to a pH value of 7.2. The total amount of ammonium hydroxide of parts 2 and 4 was sufficient to neutralize approximately 90% by weight of the methacrylic acid component of the interpolymer. The resulting mixture was agitated at 120 R. P. M. for 70 minutes without either supplying heat or accelerating the cooling. Thereafter the product was cooled to room temperature and filtered to remove any coarse foreign matter, such as polymer skins.

The drawing showing a diagrammatic flow-sheet of the invention process is representative of the steps in the process described above for the preparation of the product of Example 3. The flow sheet indicates the operation of the example single stage ammoniacal neutralizer which can be in place in place of the preferred two stages of ammoniacal neutralization. The flow sheet also indicates the optional second stage of addition of sodium lauryl sulfate dispersing agent which is described in the preparation of the product of Example 4.

Alternatively, the process for preparing the product of Example 3 can consist of the indicated steps without cooling and storing the intermediate product. The filtered product of the first-stage ammoniacal neutralization can be transferred warm or hot to the final product mixer for blending with the heat-reactive phenol/formaldehyde resin, second-stage ammoniacal neutralization and heating treatment for stabilizing the viscosity.

The resulting stabilized product exhibited excellent package-stability and viscosity-stability stored at 4.5° C. (40° F.) and 25° C. respectively for one year and stability for at least 8 months when stored at 50° C.

For use as a wire coating, the resulting product of Example 3 having a non-volatile content of 32.5% by weight as determined by weighing the residue after heating a 1 gram sample for two hours at 105° C., was adjusted to a pH of 9.3, and diluted with deionized water to a non-volatile content of 21% by weight. This ammoniacal aqueous dispersion wire enamel composition was applied to No. 18 A. W. G. copper wire in six coats at a coating speed of 14 feet per minute using a conventional vertical dip-coating bath for the aqueous enamel.

Prior to each immersion of the wire into the coating bath, it was pre-wet by immersion in a 1% aqueous solution of sodium lauryl sulfate serving as a wetting agent to facilitate wetting of the copper wire with the aqueous dispersion wire enamel. After each withdrawal from the enamel coating bath, the coated wire was heated by passing it through an oven having an average air temperature of about 221° C. (430° F.). The path of the coated wire through the oven was 12 feet in length; hence each successive coat of enamel was subjected to about 51 seconds' exposure to the oven temperature. The six coats of enamel increased the diameter of the wire by
3 mils, that is, the thickness of the coating on the copper substrate was 1.5 mils.

Another sample of the same No. 18 copper wire was coated at a coating speed of 26 feet per minute using the same aqueous dispersion wire enamel composition adjusted to a pH value of 9.3 with ammonium hydroxide and diluted with deionized water to a non-volatile content of 13% by weight. The successive coats of applied enamel were cured by passage through an oven having an average air temperature of 315° C. (600° F.) and a heating path of 12 feet. Each successive coat was exposed for about 28 seconds to the oven temperature. At the indicated coating speed and non-volatile content of the aqueous composition, the 6 coats of cured wire enamel increased the diameter of the wire by 3 mils.

A sample of No. 25 A. W. G. copper wire was also coated with 4 coats of the product of Example 3 similarly adjusted to a pH value of 9.3 and diluted to a non-volatile content of 15% by weight with deionized water. This aqueous composition was applied at a coating speed of 35 feet per minute and the successive coats were each cured by passage through a path of 4 feet in an oven having an average air temperature of 455° C. (850° F.). Each successive coat was exposed for about 7 seconds to this oven temperature. The four coats of wire enamel increased the diameter of the wire by 2 mils.

The resulting respective samples of coated wire were evaluated in accordance with NEMA and other standardized tests accepted and used by the electrical industry and were found to be equivalent to control samples of wire coated in the same manner using the equivalent aqueous dispersion interpolymer wire enamel composition which had not been subjected to ammonium neutralization and heat-treatment in accordance with the practice of this invention. Wires coated with the product of Example 3 exhibited a smoother surface than that of the insulating coating on the control wire. The product of Example 3 was castable on wire at higher speeds without depositing a rough uneven coating on the wire in comparison with the control enamel.

Copper wire coated with the product of Example 3 was successfully used in winding motors and transformers. The resulting wire was found to be particularly serviceable in the presence of fluorinated refrigerants, such as Freon-22 monochlorodifluoromethane.

The product of Example 3 was also satisfactorily applied to square and rectangular cross-section copper wire as well as to the conventional wire of circular cross-section.

**EXAMPLE 4**

<table>
<thead>
<tr>
<th>Parts by wt.</th>
<th>63.93</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water, deionized</td>
<td>0.02</td>
</tr>
<tr>
<td>Sodium metal bisulfite</td>
<td>11.87</td>
</tr>
<tr>
<td>Sodium lauryl sulfate, &quot;Duponol&quot; C solution, 25% by wt. in water</td>
<td>0.02</td>
</tr>
<tr>
<td>Acrylonitrile monomer, inhibitor free</td>
<td>1.69</td>
</tr>
<tr>
<td>Methacrylic acid monomer, 1000 p. m. hydroquinone</td>
<td>20.33</td>
</tr>
<tr>
<td>Butyl acrylate monomer, 100 p. m. hydroquinone</td>
<td>1.15</td>
</tr>
<tr>
<td>Potassium persulfate solution, 7.0% by wt. in water</td>
<td>0.65</td>
</tr>
<tr>
<td>Sodium lauryl sulfate, &quot;Duponol&quot; C solution, 25% by wt. in water</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The components of this composition were the same as those used in the preceding examples. The mixture of monomers corresponded to 35% acrylonitrile, 5% methacrylic acid and 60% butyl acrylate for a total of 100% by weight of the mixture of monomers.

The process of preparing the interpolymer by emulsion polymerization followed the process described in Example 1, initially charging all but the last two components into a homogenizing mixer to emulsify the charge and transferring the emulsion to the reactor. The charge was heated to about 60° C. and the potassium persulfate was added, initiating an exothermic reaction. Heat liberated during this reaction which lasted about two hours was withdrawn to maintain the temperature at about 60° C. Fifteen minutes after the addition of the potassium persulfate, the second addition of sodium lauryl sulfate was made. Addition of the sodium lauryl sulfate was made in two stages in order to moderate the reaction rate and to control the particle size of the resulting dispersion. After the exothermic reaction subsided, the composition was maintained at about 60° C. for one hour, neutralized at this temperature with ammonium hydroxide to a pH value of 6.0, heated to a temperature of 75° C., held at this temperature for one hour and cooled to room temperature.

The resulting aqueous dispersion interpolymer product had an average particle diameter of about 0.11 micron. The polymer had a relative viscosity of about 3.8. This product was viscosity-stable and storage-stable over a period of at least 9 months at room temperature.

The product of Example 4 was successfully used to impregnate mats of non-woven fibers of "Orlon" acrylic fiber laid down as a waterleaf by paper-making methods. The resulting dry web impregnated with 26% by weight of the interpolymer derived from the aqueous composition and weighing 3.8 grams total for an 8"×8" square was found to provide almost 100% greater bursting strength and 60% greater tear strength than conventional Kraft paper of the same weight, when tested by Tappi Standard Methods T-403 M-53 and T-414 M-49.

This product was also used to impregnate a mat of non-woven glass fibers which initially weighed 4 ounces per square foot. The weight ratio of fiber to the interpolymer binder was 1.6 to 1.0 of binder. The resulting impregnated mat was dried for 30 minutes at 107° C. (225° F.) and thereafter pressed at 50 p. s. i. for 10 minutes at 205° C. (400° F.). The resulting product was a rigid panel about 0.045 inch thick. This rigid structure exhibited high dielectric strength and was useful as slot-liners for motors and generators. The rigid structure was also useful as structural paneling where resistance to solvents and vapors was required. Solvent resistance was enhanced for these impregnated structural units where the aqueous dispersion composition of Example 4 included 5% to 10% of a water-dilutable heat-reactive phenol/formaldehyde resin such as BR-15100 based on the weight of the interpolymer.

While the specific examples describe preferred viscosity-advanced ammonial aqueous dispersion tripolymers derived from acrylonitrile, butyl acrylate, and methacrylic acid monomers as representative of the practice of the invention, numerous other aqueous dispersions of the acidic interpolymers of acrylonitrile can be similarly stabilized and viscosity-advanced in the ammonium salt form. For example, the acidic monomer component of the interpolymer can be any alpha olefinic monocarboxylic acid selected from the group consisting of methacrylic acid, acrylic acid, ethylacrylic acid, phenyl acrylate and ericotic acid or mixtures thereof. Any of these acidic monomers can be substituted on an equal weight basis for the methacrylic acid monomer used in the preparation of the described interpolymers in the examples. The acidic monomer component can be present in any amount ranging from about 1.5% to 15%, preferably about 2% to about 10% by weight based on the total weight of the mixture of monomers. Among these acidic components, methacrylic acid is particularly preferred.

While the particularly preferred ester monomer component of the acidic interpolymer is butyl acrylate, other esters of acrylic acid with a saturated aliphatic monohydric alcohol having from 1 to 12 carbon atoms can be substituted wholly or in part for the indicated amount of butyl acrylate monomer in the preparation of the inter-
polymers described in the examples. Other acidic inter-

polymers operative in the practice of this invention can
also be prepared from monomer mixtures in which the ester monomer component, present in an amount ranging from 15% to 65% by weight of the monomer mixture, is at least one ester of a saturated aliphatic mono-

hydric alcohol having from 1 to 12 carbon atoms with an alpha olefinic monocarboxylic acid selected from the group consist-
ing of acrylic acid, methacrylic acid, ethylic acid, phenyl acrylic acid and crotonic acid. Representative 1 to 12 carbon atom alcohols include methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, isobutyl alcohol, hexyl alcohol, cyclohexyl alcohol, octyl alcohol and lauryl alcohol.

The acrylonitrile monomer content of the monomer mixture used in the preparation of the acrylic acrylonitrile interpolymer can range from 30% to 80% by weight.

The emulsion polymerization in the preparation of the interpolymers can be carried out by any conventional emulsion methods, using a redox initiator. The bisulfite/per-
sulfate redox initiator mixture is particularly preferred. While the weight ratio of potassium persulfate to sodium meta bisulfite can range from 1:1 to 10:1, optimum re-
sults are obtained when the ratio is about 2 to 5 parts of the persulfate per part of the bisulfite. The preferred proportion of the redox initiator mixture is in the range of about 0.5 part to about 10.0 parts per million of the charge is preferred. Trace copper contamination functions similarly. Raw materials used ordinarily provide total amounts of iron and copper
within this preferred range. At iron and copper trace concentrations lower than 0.5 p. p. m., the exothermic reaction time of polymerization is significantly extended and at concentrations higher than 10.0 p. p. m., activation becomes too accelerated to be practical at 60° C.

However, this accelerated activation of the redox initiator can be used to advantage when the polymerization is carried out at lower temperatures.

While 60° C. is a particularly preferred operating tem-

perature for carrying out the emulsion polymerization,
temperatures in the range of 50° C. to 70° C. are ordi-
narily most suitable. The polymerization can be carried out at room temperature and at temperatures as low as about 0° C., above the freezing temperature. Tem-

peratures higher than 70° C. can be used, but operations must be carried out under pressure when the temperature ex-
ceeds the boiling point of any one of the monomers. The reactions are difficult to control at these higher tempera-
tures.

The dispersing agent used in the emulsion polymeriza-
tion is preferably sodium lauryl sulfate and is preferably used in the proportions of 0.30% to 1.50% based on the weight of the mixture of monomers. However, a propor-
tion in the range of 0.2% to 4.0% on said basis is opera-
tive. Other alkali metal salts of fatty alcohol sulfates, non-ionic dispersing agents and mixtures thereof can be used in place of the sodium lauryl sulfate.

In the described examples, the emulsion polymerization was carried out in the presence of the amount of hydro-
quinone inhibitor ordinarily present in the monomers as purchased, that is, the total hydroquinone content was in the range of about 25 to 40 p. p. m. based on the total charge. However, polymerization is operative over the range of 0 to 100 parts of hydro-
quinone per million of charge. Inhibitor-free monomers of butyl acrylate and methacrylic acid can be obtained by vacuum distillation. A concentration of the inhibitor greater than 40 p. p. m. causes a lengthening of the exo-

thermic reaction time and a decrease in the relative vis-
cosity of the interpolymer. Monomethyl ether of hydro-
quinone is occasionally used in place of hydroquinone as a polymerization inhibitor. No distinction is observed between the use of this inhibitor and hydroquinone.

Beta-bis-imino-dipropionitrile

(CH2—CH—CN)2NH

was the major component of the organic amine mixture used to inhibit one commercial grade of acrylonitrile monomer in an amount ranging from 250 to 300 p. p. m.
based on the monomer. This inhibitor significantly re-
terred the redox initiated polymerization. While the polymerization is operable in the presence of this amount of inhibitors contributed by the inhibited acrylo-
nitrile monomer, complete removal of this inhibitor is preferred. Removal of the inhibitors is best accom-

plished by passage of this amine-inhibited acrylonitrile monomer through a column of ion-exchange resin "Amberlite" IR-120 regenerated to H-form (acid form).

Alternatively, the amine inhibitors can be removed by adding 1% of orthophosphoric acid to the acrylonitrile monomer to react with the amine and thereafter distilling the acrylonitrile at atmospheric pressure.

The monomer concentration in the aqueous polymeriz-

able charge is preferably in the range of 25% to 45% by weight. While higher concentrations up to 70% are operable, coagulation losses make operations at concentra-
tions above 50% impractical or prohibitive.

The water specified in the examples is preferably of distilled, deionized or deionized quality. This is to

eliminate or minimize the effect of chemical compounds normally present in tap water on the polymerization re-
action. Tap water having a low content of such comp-
ounds can be used.

Agitation during emulsion polymerization is preferably carried out within the range of 150 to 300 R. P. M., but any speed which provides adequate heat transfer and

maintains uniform dispersion of the monomers in the aqueous emulsion is operative. Ordinarily this requires agitation at a speed within the range of 50 to 400 R. P. M.

Higher speeds are undesirable because many interpolymer
dispersions coagulate or coalesce under mechanical shear.

The polymerization charge is preferably emulsified as a homo
geneous premix prior to adding into the poly-

merization reactor. A particularly suitable homogenizer
for premixing is the Eppenbach homo-mixer. The model of this mixer used was comprised of a multi-bladed rotor having a rotor/stator clearance in the range of about .030 to about .0625 inch and rotated with a peripheral speed of about 60 feet per second. A homogeneous premix ordi-
narily is stable against phase separation for at least
about 60 minutes at 60° C. Hence, agitator speed in the polymerization reactor is less critical and serves pri-

marily to provide good heat transfer when the process
includes the step of high speed homogenous premixing.

The polymerization reaction period is preferably in the range of 75 to 150 minutes, as measured by the duration of the exothermic reaction, to assure adequate heat-transfer.

Rate of heat dissipation ordinarily provided in com-

mercial operations practically limits the exothermic period to at least 60 minutes in commercial operations. The exothermic reaction periods beyond about 6 hours are con-
sidered to be impractically long.

Aqueous dispersion interpolymer, as represented by Examples 1, 2 and 3 prepared by emulsion polymeriza-
tion under the aforementioned preferred operating con-
ditions, ordinarily have a particle size in the range of about 0.03 to .30 micron and the interpolymer is char-
acterized by a weight average molecular weight, as deter-
imed by light scattering, in the range of about 300,000 to 800,000. The relative viscosity of these interpolymers based on a 0.5% solution in dimethylformamide ordi-
narily ranges from about 4.0 to 10.0.

Emulsion polymerized interpolymers derived from monomer mixtures in which the weight proportion of the acrylic ester predominates over the acrylonitrile, as
represented by Example 4, ordinarily are characterized by a relative viscosity in the range of 2.5 to 5.0 in dimethylformamide and the average particle size of the interpolymer in the aqueous dispersion is in the range of about 0.5 to 1.5 micron.

In neutralizing the acidic aqueous dispersion interpolymer compositions with ammonium hydroxide to provide the composition with viscosity-stability, resistance to gelation and package-stability, a sufficient amount of ammonium hydroxide is added to the acidic aqueous dispersion, which ordinarily is at a pH value no greater than about 4.0, to increase the pH value to at least about 5.5. This amount of ammonium hydroxide ordinarily added to reach this pH value is sufficient to convert at least 10% by weight of the acidic component of the interpolymer to its ammonium salt. At a pH value in the range of 5.5 to 6.5, the ammoniacal aqueous dispersion composition is not highly advanced in viscosity over the unneutralized acidic aqueous dispersion and it is most convenient to separate undesirable coagulum and fine-particle-size polymer grit from the dispersion at this ammoniacal stage, such as by filtration.

If separation of the coagulum and polymer grit is delayed until after ammoniacal heat-treatment at a higher pH value, such as in the range of 6.7 to 8.0, whereby the viscosity is significantly advanced, the final stage of the coagulum and polymer grit is more difficult to accomplish by ordinary means practical for commercial operations. If the separation is carried out with the acidic aqueous dispersion prior to the stabilizing ammoniacal neutralization to a pH value of at least 5.5, polymer grit and coagulum continues to form during storage under acidic conditions corresponding to a pH value less than 5.5. Hence, in commercial operations, two stage ammoniacal neutralization is preferred with a separation or filtration step between the two ammoniacal stages. In the initial stage, the ammoniacal neutralization is carried out to a pH value of 5.5 to 6.5 and in the second stage the ammoniacal neutralization is advanced to a pH value in the range greater than that of the first stage up to 8.0, preferably in the range of 6.7 to 7.5. The total amount of ammonium hydroxide ordinarily added is sufficient to convert from 50% to about 100% by weight of the acidic component of the interpolymer to ammonium salt.

Under operating conditions which provide for ammoniacal heat-treatment of the acidic aqueous dispersion interpolymer immediately after polymerization, the addition of ammonium hydroxide can be made as a single stage, operating the coagulum and polymer grit from the acidic composition prior to the ammoniacal neutralization.

In the heat-treatment of the ammoniacal aqueous dispersion interpolymer composition, the temperature can range from about 45°C to about 95°C. The heating period can range from about 3 minutes to about 4 hours. The preferred heat-treatment ranges from about 15 minutes to about 120 minutes at a temperature ranging from about 65°C to about 90°C. Heating for a period as short as 5 minutes within these temperature ranges ordinarily provides viscosity-advancement of at least 50% over that of the untreated aqueous dispersion.

When ammoniacal neutralization is in two stages, heating in the initial neutralization stage is not critical as viscosity-advancement is not the primary object of the initial stage. In this initial ammoniacal neutralization, the ammonium hydroxide can be added at the temperature of the emulsion or at a temperature of the emulsion polymerization, this temperature being in the range of room temperature to about 70°C and ordinarily at least about 45°C. The second stage ammoniacal neutralization to a pH value in the range of 6.7 to 8.0 accompanied with further heating represents the pertinent viscosity-advancement stage.

When the aqueous interpolymer dispersion is modified with water-dilutable heat-reactive aldehyde condensation resins, such as a heat-reactive phenol/formaldehyde resin, the modifier can be blended with the interpolymer dispersion either before or after the ammoniacal heat-treatment or between the first and second stage of ammoniacal neutralization. Blending prior to the heat-treatment is preferred as the entire composition is thereby stabilized rather than just the component interpolymer dispersion. The particularly preferred method of preparing the final enamel from the acidic aqueous dispersion interpolymer composition and the heat-reactive aldehyde condensation resin includes the steps of first stage ammoniacal neutralization of the acidic dispersion at a temperature in the range of 45°C to 65°C to a pH value of 5.5 to 6.5, filtering, blending the partially neutralized aqueous dispersion with the heat-reactive aldehyde condensation resin, second stage ammoniacal neutralization to a pH value in the range of 6.7 to 7.5, heating at a temperature in the range of 65°C to 90°C to viscosity-advance the composition and cooling to room temperature. Ordinarily the final product is filtered to remove any coarse coagulum formed by drying out of interpolymer dispersion on parts of the heat-treating equipment.

While the examples illustrate modification of the acrylonitrile interpolymer dispersion with a water-dilutable heat-reactive phenol/formaldehyde resin, other water-dilutable, heat-reactive aldehyde condensation resins selected from the group consisting of urea/formaldehyde resin, melamine/formaldehyde resin, urea/melamine/formaldehyde resin, phenol/formaldehyde resin, and mixtures thereof can be substituted on an equal weight basis for the phenol/formaldehyde resin in the examples. When these heat-reactive resins are used to modify the interpolymer dispersion, the amount can vary from about 2% to about 40% based on the weight of the interpolymer. A proportion of these resins in the range of 5% to 20% on the indicated basis is preferred.

Water-soluble coalescing agents are desirable components of the aqueous dispersion compositions when applied at room temperature as an air-drying coating or impregnant. The presence of a coalescing agent ordinarily is not required where the applied coating is baked at high temperatures sufficient to bring about coalescence.

The content of acrylonitrile in the interpolymer has a pertinent effect on the need for a coalescing agent. When the acrylonitrile content is low, ordinarily there is no need for the coalescing agent, but when the acrylonitrile content is high, such as 65% to 80% by weight of the interpolymer, a coalescing agent is required in applications where the dry coating is not baked. Cyclic ethylene carbonate, tetramethylene sulfone, ethylene glycol monoethers of 1 to 4 carbon atom saturated aliphatic monohydric alcohols, diethylene glycol monoethers of 1 to 4 carbon atom saturated aliphatic monohydric alcohols, diacetone alcohol, dimethylformamide and dimethylacetamide are representative water-soluble coalescing agents which can be included in the aqueous dispersion interpolymer composition. The amount of water-soluble coalescing agent can be proportioned amounts up to 150% based on the weight of the dispersed interpolymer in the final composition, but ordinarily the presence of the coalescing agent is avoided during the ammoniacal heat-treatment step.

The stabilized aqueous dispersion interpolymer compositions can be further modified with pigments, fillers, extenders; finely-divided water-dispersible hydrosilicates such as bentonite and montmorillonite clay; and compatible film-forming resins and plasticizers. If desired, the compositions of this invention can be adjusted at the time of use to a higher ammoniacal pH value in the range of 8.0 to 10.0 with ammonium hydroxide or volatile amines. In some applications, this higher alkalinity provides improved wetting of the substrate.
The aqueous dispersion compositions of this invention can contain as much as 50% by weight of dispersed ammonium salt of an acidic interpolymer and as little as 5%. Ordinarily the practical content of ammonium interpolymer is in the range of 10% to 45% by weight.

These aqueous dispersion interpolymer compositions can be applied by any of the conventional methods ordinarily used in coating or impregnating with aqueous dispersion process. The applied coatings or impregnants can be dried or cured at temperatures ranging from room temperature to baking temperatures as high as 500° C.

The stabilized aqueous dispersion interpolymer compositions have wide utility in the coating and impregnating fields. They provide excellent baking finishes for electrical wire insulation. They provide excellent air-drawing finishes for wood, such as on bowling alloys and bowling pins. They can be applied to metallic and non-metallic substrates either as baking or air-drying finishes. They are particularly useful as impregnants for fabrics and non-woven webs prepared from synthetic fibers such as derived from polyacrylonitrile, ethylene terephthalate polyester polymers, nylon, viscose rayon, polyurethane, polytetrafluoroethylene and polyvinylidene chloride. They can also be used to coat or impregnate products prepared from natural fibers such as cotton, jute, ground wood pulp and chemical wood pulp. They are also useful for coating and impregnating woven fabric and non-woven webs prepared from glass fibers. When used as the impregnant for non-woven webs, the proportion of dry weight impregnant to fiber can be varied to provide useful products ranging in properties from those of thin paper-like sheets or leather-like products to thick rigid panels.

This invention offers a significant advance in the art in providing commercially acceptable ammoniacal aqueous dispersion interpolymer salt compositions which are characterized by package-stability, gelation-resistance and viscosity-stability. This invention also provides for the preparation of stable aqueous dispersion interpolymer compositions desirably advanced in viscosity.

While there are above disclosed but a limited number of embodiments of the structure, process and product of the invention herein presented, it is possible to produce still other embodiments without departing from the spirit and scope of this invention which has been described and, it is desired therefore that only such limitations be imposed on the appended claims as are stated herein, or required by the prior art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for preparing a package-stable and gelation-resistant aqueous dispersion interpolymer composition which process comprises preforming, by emulsion polymerization in water, an acidic interpolymer of a mixture of monomers consisting of (A) 30% to 80% by weight of acrylonitrile, (B) 1.5% to 15% by weight of at least one alpha olefinic monocarboxylic acid selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, phenyl acryl acid and crotonic acid, and (C) 15% to 65% by weight of at least one ester of an acid with a saturated aliphatic monohydric alcohol having from 1 to 12 carbon atoms, forming an ammonium salt of said interpolymer by reacting the acidic (B) component of the interpolymer with ammonium hydroxide at a temperature in the range of about 45° C. to about 95° C., and cooling the ammoniacal dispersion to a temperature below about 30° C., the amount of ammonium hydroxide introduced being sufficient to provide the aqueous dispersion with a pH value in the range of 5.5 to 8.0.

2. The process of claim 1 wherein said ammoniacal reaction mixture is maintained within said temperature range for a period ranging from 5 minutes to 4 hours prior to cooling, whereby a stable advance in viscosity is imparted to the aqueous dispersion.

3. The process of claim 1 wherein the amount of ammonium hydroxide is sufficient to form an ammonium salt corresponding to reaction with at least 10% by weight of the acidic (B) component of the interpolymer.

4. The process of claim 1 wherein the amount of ammonium hydroxide is sufficient to form an ammonium salt corresponding to reaction with at least 50% by weight of the acidic (B) component of the interpolymer.

5. The process of claim 1 wherein said mixture of monomers consists of acrylonitrile, methacrylic acid and butyl acrylate.

6. The process of claim 1 wherein said ammoniacal reaction is carried out in two stages with a separation step between the initial stage and the second stage, to remove coagulum and polymer grit, the reaction in said initial stage being at a pH value in the range of 5.5 to 6.5, the second stage reaction subsequent to said separation step being carried out at a temperature in the range of 45° C. to 95° C. with sufficient ammonium hydroxide being present to provide the aqueous dispersion with a pH value in the range of greater than that of the first stage up to 8.0.

7. The process of claim 6 which includes, prior to said second stage ammoniacal reaction, the step of blending with the aqueous dispersion interpolymer composition, a water-dilutable, heat-reactive aldehyde condensation resin selected from the group consisting of phenol/formaldehyde resin, urea/formaldehyde resin, melamine/formaldehyde resin, urea/melamine/formaldehyde resin and mixtures thereof in an amount ranging from about 2% to 40% based on the weight of said interpolymer.

8. The process of claim 7 wherein said water-dilutable, heat-reactive aldehyde condensation resin is phenol/formaldehyde resin.

9. The process of claim 6 which includes, subsequent to said initial stage of ammoniacal reaction and prior to said second stage of ammoniacal reaction the step of blending with the aqueous dispersion interpolymer composition, a water-dilutable, heat-reactive aldehyde condensation resin selected from the group consisting of phenol/formaldehyde resin, urea/formaldehyde resin, melamine/formaldehyde resin, urea/melamine/formaldehyde resin and mixtures thereof in an amount ranging from about 2% to 40% based on the weight of said interpolymer.

10. The process of claim 9 wherein the heat-effected ammoniacal reaction of said second stage is carried out by heating at a temperature in the range of 65° C. to 90° C. for 15 to 120 minutes.

11. A process for preparing a gelation resistant, viscosity-stable and package-stable aqueous dispersion interpolymer composition which process comprises the steps of forming a homogeneous premix composition comprising water, sodium lauryl sulfate, sodium meta bisulfite and a mixture of monomers consisting of (A) 30% to 80% by weight of acrylonitrile, (B) 1.5% to 15% by weight of methacrylic acid, and (C) 15% to 65% by weight of at least one ester of an acid with a saturated aliphatic monohydric alcohol having from 1 to 12 carbon atoms, forming an ammonium salt of said interpolymer by reacting the acidic (B) component of the interpolymer with ammonium hydroxide at a temperature in the range of about 45° C. to about 95° C., and cooling the ammoniacal dispersion to a temperature below about 30° C., the amount of ammonium hydroxide introduced being sufficient to provide the aqueous dispersion with a pH value in the range of 5.5 to 8.0.

12. The process of claim 1 wherein said ammoniacal reaction mixture is maintained within said temperature range for a period ranging from 5 minutes to 4 hours prior to cooling, whereby a stable advance in viscosity is imparted to the aqueous dispersion.

13. The process of claim 1 wherein the amount of ammonium hydroxide is sufficient to form an ammonium salt corresponding to reaction with at least 10% by weight of the acidic (B) component of the interpolymer.

14. The process of claim 1 wherein the amount of ammonium hydroxide is sufficient to form an ammonium salt corresponding to reaction with at least 50% by weight of the acidic (B) component of the interpolymer.

15. The process of claim 1 wherein said mixture of monomers consists of acrylonitrile, methacrylic acid and butyl acrylate.

16. The process of claim 1 wherein said ammoniacal reaction is carried out in two stages with a separation step between the initial stage and the second stage, to remove coagulum and polymer grit, the reaction in said initial stage being at a pH value in the range of 5.5 to about 6.5, the second stage reaction subsequent to said separation step being carried out at a temperature in the range of 45° C. to 95° C. with sufficient ammonium hydroxide being present to provide the aqueous dispersion with a pH value in the range of greater than that of the first stage up to 8.0.

17. The process of claim 6 which includes, prior to said second stage ammoniacal reaction, the step of blending with the aqueous dispersion interpolymer composition, a water-dilutable, heat-reactive aldehyde condensation resin selected from the group consisting of phenol/formaldehyde resin, urea/formaldehyde resin, melamine/formaldehyde resin, urea/melamine/formaldehyde resin and mixtures thereof in an amount ranging from about 2% to 40% based on the weight of said interpolymer.

18. The process of claim 7 wherein said water-dilutable, heat-reactive aldehyde condensation resin is phenol/formaldehyde resin.

19. The process of claim 6 which includes, subsequent to said initial stage of ammoniacal reaction and prior to said second stage of ammoniacal reaction the step of blending with the aqueous dispersion interpolymer composition, a water-dilutable, heat-reactive aldehyde condensation resin selected from the group consisting of phenol/formaldehyde resin, urea/formaldehyde resin, melamine/formaldehyde resin, urea/melamine/formaldehyde resin and mixtures thereof in an amount ranging from about 2% to 40% based on the weight of said interpolymer.

20. The process of claim 9 wherein the heat-effected ammoniacal reaction of said second stage is carried out by heating at a temperature in the range of 65° C. to 90° C. for 15 to 120 minutes.

21. A process for preparing a gelation resistant, viscosity-stable and package-stable aqueous dispersion interpolymer composition which process comprises the steps of forming a homogeneous premix composition comprising water, sodium lauryl sulfate, sodium meta bisulfite and a mixture of monomers consisting of (A) 30% to 80% by weight of acrylonitrile, (B) 1.5% to 15% by weight of methacrylic acid, and (C) 15% to 65% by weight of butyl acrylate, emulsion-polymerizing said homogeneous premix in the presence of potassium persulfate added to complete in combination with the bisulfite a redox initiator, forming an ammonium salt of the acidic interpolymer by adding ammonium hydroxide to the resulting aqueous dispersion of the acidic interpolymer to a pH value in the range of 5.5 to 6.5 as a first stage ammoniacal reaction, filtering the resulting ammoniacal aqueous dispersion, mixing said filtered dispersion with a water-dilutable, heat-reactive phenol/formaldehyde resin and further adding ammonium hydroxide to the resulting mixture to a pH value in the range of about 6.7 to about 7.5 as a second stage ammoniacal reaction, maintaining the product of said second stage reaction at a temperature in the range of 65° C. to 90° C. for a period ranging
from 15 minutes to about 120 minutes and cooling to a temperature below about 30° C.

12. The process of claim 11 wherein the amount of ammonium hydroxide added in the first stage ammoniacal reaction is sufficient to convert at least 10% by weight of the methacrylic acid component (B) of the interpolymer to its ammonium salt and the total amount of ammonium hydroxide added in the first and second stages of ammoniacal reaction is sufficient to convert at least 50% by weight of the methacrylic acid component (B) of the interpolymer to its ammonium salt.

13. The process of preparing a package-stable, gelation-resistant, heat-bodied aqueous dispersion interpolymer composition comprising the steps of: (a) preforming an aqueous acidic interpolymer dispersion composition by initially preparing an aqueous dispersion polymerization charge consisting essentially of water, a mixture of polymerizable monomers consisting of (A) 30% to 80% acrylonitrile, (B) 1.5% to 15% of at least one alpha olefinic monocarboxylic acid selected from the group consisting of acrylic acid, methacrylic acid, ethacrylic acid, phenyl acrylic acid and crotonic acid, and (C) 15% to 65% of at least one ester of an acid of (B) with a saturated aliphatic monohydric alcohol having from 1 to 12 carbon atoms per molecule, and from .2% to 4% of an alkali metal salt of an acidic fatty alcohol sulfate ester based on the weight of said polymerizable monomers, the concentration of said mixture of monomers being from about 25% to about 50% of said aqueous charge, and effecting polymerization of said polymerizable monomers the presence of about 25% to 1% of a vinyl polymerization initiator based on the weight of said monomers at a temperature from about 50° C. to about 70° C. for a period sufficient to provide the resulting interpolymer with a relative viscosity of from about 2.5 to 10 based on a 0.5% solution in dimethyl formamide, (b) forming an ammonium salt of said dispersed acidic interpolymer resulting from step (a) by adding ammonium hydroxide thereto in an amount sufficient to adjust said aqueous interpolymer dispersion to a pH value of 5.5 to 6.5 and reacting the resulting mixture at a temperature from about 45° C. to about 70° C., (c) filtering the product of step (b), the aqueous dispersion of said interpolymer ammonium salt being the filtrate, (d) further adding ammonium hydroxide to said filtered dispersion in an amount sufficient to adjust said aqueous dispersion to a pH value of 6.7 to 8, (e) heating the product aqueous dispersion of the resulting interpolymer ammonium salt at a temperature from 65° C. to 90° C. for a period of about 15 to 120 minutes, and (f) cooling the product dispersion to room temperature below 30° C.


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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,866,763

December 30, 1958

Philip F. Sanders

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 68, for "A. E. T. M." read -- A. S. T. M. --; column 6, line 40, for "26,10" read -- 26,10 --; column 7, line 48, for "6% by wt." read -- 66% by wt. --; column 11, line 27, for "50%" read -- .50% --; column 15, line 17, for "drawing" read -- drying --; column 18, line 1, for "25%" read -- .25% --.

Signed and sealed this 21st day of April 1959.

(SEAL)
Attest:
KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents