A surface sizing composition for paper which comprises a copolymer of styrene and at least one unsaturated carboxylic compound selected from the group consisting of maleic acid, maleic anhydride and half-esters of maleic acid, wherein the copolymer has a carboxylate equivalent of 80 – 300 based on the free carboxylic acid form, and wherein the copolymer has 5 – 50% of its total carboxylic groups as alkali metal salts and 95 – 50% of its total carboxylic groups as at least one non-metal salt selected from the group consisting of ammonium salts and lower alkyl amine salts.

14 Claims, No Drawings
SURFACE SIZING COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to surface sizing compositions for paper making. More particularly, this invention relates to stable surface sizing compositions which have excellent heat, mechanical and alum resistance during surface sizing. As used herein the term "carboxylic group" is intended to include carboxylate salts and the anhydride structure in addition of course, to the free carboxylic acid group. Of course, an anhydride group is the group which results from the condensation of two carboxylic groups.

2. Description of the Prior Art

Surface sizing compositions are usually applied to paper in a size press. Different types of size presses are used according to how the rolls of paper are arranged and the method by which sizing solution is applied to the paper. Vertical size presses are made up of top and bottom rolls located one over the other, and horizontal size presses consist of two rolls placed side by side. Recently, inclined size presses have been principally used which contain two rolls placed obliquely, and which apply sizing solution to the paper by placing the sizing solution into the dam formed by the two rolls.

Paper is commonly surface-sized by means of a size press as follows: The paper sheet is semi-dried beforehand or is dried by driers positioned just before the size press runs through the dam of the sizing solution at a high speed. It is run between two press rolls under a high nip pressure, and then the treated sheet is dried by driers which are located just beyond the size press.

Surface sizing has some advantages. For example, it leads to substantial savings in sizing costs and to improvement in paper quality compared to internal sizing techniques because almost all of the sizing composition is retained on the surface of the paper during surface sizing. During surface sizing by the size press, however, the sizing solution suffers heat and mechanical shock which is generated during the operation. In addition, aluminum salts such as alum eluted from the paper into the sizing solution. These salts are used in the wet end of the sheeting step. These eluted salts have some adverse effects on the sizing solution because they facilitate precipitation of materials from the sizing solution. Because of the operational difficulties encountered in the sizing process, the sizing agent which is the main ingredient of the sizing solution should be stable to heat mechanical shock and be able to resist the aluminum salts in order to give the paper the proper amount of water resistance and writing quality.

Heretofore, various surface sizing compositions have been proposed and used. They have not been satisfactory, although some of them have a few advantages. In continuous sizing operations, sizing solutions which contain conventional sizing compositions gradually lose their solubilizing properties because of the heat, mechanical shock and aluminum salts to which they are exposed. This gradually results in the formation of scum. The presence of the scum causes a decrease in the sizing effect of the sizing solution, and has an adverse effect on the appearance of the treated paper because of the presence of the scum on the surface of the paper. Because of these disadvantages surface sizing compositions have enjoyed limited use in the field of paper making.

A need, therefore, continues to exist for a surface sizing composition which has none of the disadvantages of the prior art sizing compositions and which is stable to mechanical shock and heat.

SUMMARY OF THE INVENTION

Accordingly, one object of this invention is to provide a surface sizing composition having improved properties.

Another object of this invention is to provide a surface sizing composition having good stability under operating conditions.

Yet another object of this invention is to provide a surface sizing composition which yields paper having improved properties at low cost.

Briefly, these objects and other objects of the invention as hereinafter will become more readily apparent can be attained by a surface sizing composition which comprises a copolymer of styrene and at least one unsaturated carboxylic compound selected from the group consisting of maleic acid, maleic anhydride and half-esters of maleic acid, wherein the copolymer has a carboxylate equivalent of 80 - 300 based on the free carboxylic acid form, and wherein the copolymer has 5 - 50% of its total carboxylic groups as alkali metal salts and 95 - 50% of its total carboxylic groups as at least one non-metal salt selected from the group consisting of ammonium salts and lower alkyl amine salts.

BRIEF DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the composition of the invention the carboxylate equivalent of the copolymer as the free acid must be 80 - 300, preferably 100 - 240, wherein the carboxylate equivalent means the molecular weight of the copolymer (reduced to the free acid basis) per carboxylic group. A copolymer with a value less than 80 exhibits inadequate sizing effects, while if the copolymer has a value greater than 300 the sizing effect and the solubility of the copolymer in water decreases. When the copolymer is used under severe sizing conditions such as long continuous operation at severe pH values, it is preferred to use copolymers which have relatively low equivalents within the range of 80 to 300, because lower carboxylate equivalents bring about better solubility of the copolymer in water. Furthermore, the carboxylate groups in the copolymer must be present in the form of specific salts in order to attain the objects of this invention. Thus, 5 - 50% of the total carboxylic groups must exist as an alkali metal salt, and 95 - 50% of the total carboxylic groups must exist in the form of at least one salt selected from the group consisting of ammonium salts and lower alkyl amine salts. If the copolymer contains less than 5% alkali metal salts, the resulting copolymer does not have enough stability when used in the size press. If the copolymer has an alkali metal salt content greater than 50% the high salt content has an adverse effect on the sizing effects of the copolymer. When the sizing effects and the stability of the copolymer are considered it is preferred that the alkali metal salt be from 10 - 25%. However, if the stability characteristics of the copolymer are to be emphasized, it is preferable to use a copolymer having an alkali metal salt content within the higher regions of the 5 - 50% range. The copolymer also has a carboxylate group content as the ammonium and lower alkylamine salts preferably ranging from 90 - 75% of the total carboxylate group content. The copolymer preferably may
also have a free carboxylate group content less than 45%, less than 15% of the total carboxylate group content.

Suitable alkali metal ions include sodium, potassium and mixtures thereof. Suitable lower alkyl Cₙ₁₆ amine
salts include salts of monomethyl amine, dimethyl amine, trimethyl amine, monooethyl amine, diethyl amine, triethyl amine and mixtures thereof. Mixtures of the ammonium salt and the lower alkyl amine salts may also be used. The preferred non-metal salts are ammoneballs and salts formed from amines having a molecular weight less than 60 and a boiling point less than 20°C. (760 mmHg).

The copolymer used in this invention can be produced by a group of one or several known methods. The copolymer is generally produced by copolymerizing styrene and an unsaturated carboxylic compound selected from the group consisting of maleic anhydride, fumaric acid and half esters of maleic acid in the presence of a solvent such as toluene, and then neutralizing the resulting copolymer to form the salts. The copolymer may be alternatively produced by just copolymerizing styrene and the salts of the unsaturated carboxylic compound. Half-esterification may be conducted after the styrene and maleic anhydride or maleic acid are copolymerized. Suitable alcohols for the esterification reaction include monohydric aliphatic alcohols containing 1 - 20 carbon atoms and having a straight or branched chain or an alicyclic ring. The preferred alcohols have straight or branched chains and contain 4 - 8 carbon atoms. The mole ratio of styrene to the unsaturated carboxylic compound is generally 30 - 90 : 70 - 10, preferably 45 - 60 : 55 - 40.

The copolymer of this invention may contain one or more additional structural units. Suitable ethyleneically unsaturated monomers as the third monomer, or structural unit include monomers containing carboxylic groups such as acrylic acid, methacrylic acid and fumaric acid, vinyl monomers such as vinyl acetate, vinyl chloride and α-olefins; acrylates and methacrylates such as methyl acrylate, methyl methacrylate, butyl methacrylate, hexyl methacrylate, octyl methacrylate and octyl acrylate; and other specific acrylic monomers such as acrylamide and hydroxyethyl acrylate. Among these monomers, the preferred are acrylates and methacrylates having 4 - 12 carbon atoms. The third monomer may be present in molar amounts less than 60% preferably less than 40% of the total. When the third monomer contains a carboxylic group, the group is included in the calculation of the carboxylate equivalent and the percentage of carboxylate groups in a salt the copolymer of the invention has a viscosity of at least 1000 cps. as a 40% by weight aqueous solution at 30°C.

The surface sizing composition of this invention may consist of the abovementioned copolymer alone. However, the copolymer is generally used with modifiers such as modified starches such as oxidized starches and enzyme converted starches, and polyvinyl alcohols. The weight ratio of the copolymer to the modifier may be 0.1 - 50 : 99.9 - 50. The copolymer may be also used with conventional sizing agents and other modifiers such as rosins and petroleum resins.

The surface sizing composition of this invention may be applied to paper sheets by any conventional method. Thus, the sizing composition can be dissolved or dispersed in water to form a sizing solution (1 - 20% by weight), and then the solution is applied to a paper sheet by a size press, and the treated sheet is dried. The amount of the copolymer deposited on the paper is 0.01 - 0.5gm (solid), preferably 0.05 - 0.15gm (solid). When a modifier is used with the copolymer, the amount of sizing composition deposited on the paper is 1 - 5gm (solid), preferably 2 - 3gm (solid).

The surface sizing composition is used on various kinds of paper bases such as paper which contains a filler, water-leaf paper and soft-sized paper. The preferred paper is one which contains little or no internal sizing composition.

The surface sizing composition of this invention has a good sizing effect and good stability in the sizing solution. The sizing solution containing the sizing composition of this invention, therefore, does not form a scum even under long and severe operating conditions in size presses.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

In the examples, the viscosity was measured as a 40% by weight aqueous solution at 30°C, and the pH was measured as a 4% by weight aqueous solution.

**EXAMPLE 1**

Into a four-necked, round-bottom 1000 c.c. flask equipped with a stirrer, a reflux condenser, a dropping funnel, a thermometer and a tube for the introduction of nitrogen gas, were charged 230.8g of methyl ethyl ketone, 1.0g of lauryl mercaptan, and 45.0g of maleic anhydride. The mixture was heated at reflux with stirring under a nitrogen atmosphere. Then, to the mixture was added a solution which was obtained by dissolving 0.5g of 2,2'-azobisobutyronitrile in 26.3g of styrene and 32.4g of methyl methacrylate slowly over about 4 hours, and then the reaction mixture was kept at a reflux for an additional 2 hours. The resulting mixture was cooled to 60°C by a water bath, and then was neutralized with 37 g of a 10% by weight aqueous solution of sodium hydroxide. The resulting neutralized solution was distilled to remove methyl ethyl ketone, and then was treated with 50.3g of a 28% by weight aqueous solution of ammonium hydroxide after being cooled to 60°C. By this procedure was obtained a 40% by weight aqueous solution of the copolymer.

The resulting copolymer had a carboxylate equivalent of 109, a viscosity of about 5000 cps., and a pH of 9.5. The copolymer had 10% of its total carboxylic groups in the form of the sodium salt and 90% in the form of the ammonium salt.

**EXAMPLE 2**

Example 1 was repeated and a copolymer of the free carboxylic acid was obtained. The resulting copolymer was esterified with 29.6g of n-butyl alcohol to form a copolymer having a carboxylate equivalent of 256. Then, the resulting copolymer was neutralized in the same manner as described in Example 1 whereby a 40% by weight aqueous solution of the copolymer was obtained which had 30% of the carboxylate groups as the sodium salt and 70% of the carboxylate groups as the ammonium salt. The copolymer had a viscosity of 8000 cps. and a pH of 9.4.
EXAMPLE 3

A copolymer was produced by the same method described in Example 1 using 178.2 g of ethylene dichloride, 1.2 g of lauryl mercapta, 54.0 g of maleic anhydride, 50.4 g of styrene, 15.6 g of n-butyl acrylate and 0.6 g of 2,2'-azobisisobutyronitrile. The solution was neutralized whereby a 40% by weight aqueous solution of the copolymer which had 15% of the carboxylate groups as the potassium salt, 76% as the ammonium salt and the balance as the free carboxylic acid was obtained. Furthermore, the resulting copolymer had a carboxylic equivalent of 114, a viscosity of about 6,000 cps. and a pH of 8.2.

EXAMPLE 4

A copolymer was produced by the same method described in Example 1 using 230.8 g of toluene, 1.0 g of lauryl mercapta, 45.8 g of maleic anhydride 47.8 g of styrene and 0.5 g of 2,2'-azobisisobutyronitrile. The solution was neutralized whereby a 40% by weight aqueous solution of the copolymer which had 20% of the carboxylate groups as the sodium salt, 70% as the ammonium salt and the balance as the free carboxylic acid was obtained. The copolymer had a carboxylic equivalent of 101, a viscosity of about 9,000 cps. and a pH of 8.1.

EXAMPLE 5

Example 4 was repeated whereby a copolymer as the free acid was obtained. The resulting copolymer was neutralized whereby a 40% by weight aqueous solution of the copolymer which had 20% of the carboxylate groups as the sodium salt, 70% as the monoethyl amine salt and the balance as the free carboxylic acid was obtained. The copolymer had a viscosity of 10,000 cps. and a pH of 9.4.

EXAMPLE 6 (Test of Stability)

A stability test was conducted with each of the sizing solutions prepared from the copolymer solutions produced in Examples 1 – 5.

An aqueous sizing solution (5,000 cc) was prepared which contained 0.8% by weight of each of the copolymers of the invention and 7.2% by weight of an oxidized starch. For comparison, an aqueous sizing solution was prepared using conventional sizing agents instead of the copolymer of this invention. Each of the sizing solutions was supplied to an inclined labo-size press by a handy pump. Outflow of the solution was recycled. The stability was determined by observing the formation of scum every 30 minutes. Operational conditions were as follows:

1. Press speed: 100 m/min.
2. Nip Pressure: 20 Kg/cm.
3. Operation Time: 8 hours
4. Temperature of the solution: Adjusted to 60°C
5. pH of the solution: Aqueous alum solution 0.5% by weight was added every 60 minutes, so that the pH was adjusted to 5.0, four hours after starting.

The results of the stability tests are shown in Table 1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Surface sizing agents</th>
<th>Stability of the sizing solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Example 1</td>
<td>No scum developed in the pressing operation for more than 8 hours</td>
</tr>
<tr>
<td>2.</td>
<td>Example 2</td>
<td>&quot;</td>
</tr>
<tr>
<td>3.</td>
<td>Example 3</td>
<td>&quot;</td>
</tr>
<tr>
<td>4.</td>
<td>Example 4</td>
<td>No scum developed in the pressing operation for more than 8 hours</td>
</tr>
<tr>
<td>5.</td>
<td>Example 5</td>
<td>Substantial development of scum in the pressing operation after 0.5 hour</td>
</tr>
<tr>
<td>6.</td>
<td>Rosin size</td>
<td>(Conventional)</td>
</tr>
<tr>
<td>7.</td>
<td>Petroleum resin</td>
<td>Substantial development of scum in the pressing operation after 1.5 hours</td>
</tr>
<tr>
<td>8.</td>
<td>Styrene-maleic anhydride copolymer (conventional)</td>
<td>Substantial development of scum in the pressing operation after 3.0 – 3.5 hours</td>
</tr>
</tbody>
</table>

EXAMPLE 7 (Test of the sizing effects)

A test of the sizing effects was made on each of the copolymers produced in Examples 1 – 5 in comparison to some conventional sizing agents.

The operational conditions for sizing tests were as follows:

1. Base paper
   Paper was produced by sheeting pulp L-BKP. The pulp had a degree of beating of 420 contained clay (filler) and a fortified rosin (internal sizing agent) at a pH of 4.5 (adjusted with alum). The resulting paper had a weight of 60 – 62 g/m² with an ash content of 13.0% and a rosin content of 0.09% by weight.

2. Surface sizing solution
   | Oxidized starch | 7.6 (% by weight) |
   | Each sizing agent (active) | 0.4 |
   | Water | 92 |
   | TOTAL 100 |

3. Sizing operation
   The sizing operation was made with an inclined labo-size press at a speed of 100 m/min and a nip pressure of 10 Kg/cm.

4. Resulting paper
   The paper treated as mentioned above contained 0.1 g/m² of the sizing agent and 2.0 g/m² of the oxidized starch.

The results of the sizing effect tests are shown in Table 2.
<table>
<thead>
<tr>
<th>No.</th>
<th>Surface sizing agent</th>
<th>Sizing degree (sec.)</th>
<th>Writability</th>
<th>IGT surface strength (cm/sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Example 1</td>
<td>23.3</td>
<td>5 - 6</td>
<td>203</td>
</tr>
<tr>
<td>2</td>
<td>Example 2</td>
<td>21.1</td>
<td>5 - 6</td>
<td>184</td>
</tr>
<tr>
<td>3</td>
<td>Example 3</td>
<td>24.5</td>
<td>6</td>
<td>238</td>
</tr>
<tr>
<td>4</td>
<td>Example 4</td>
<td>23.0</td>
<td>5 - 6</td>
<td>205</td>
</tr>
<tr>
<td>5</td>
<td>Example 5</td>
<td>23.0</td>
<td>5 - 6</td>
<td>205</td>
</tr>
<tr>
<td>6</td>
<td>Rosin size (conventional)</td>
<td>20.2</td>
<td>3 - 4</td>
<td>146</td>
</tr>
<tr>
<td>7</td>
<td>Petroleum resin (Conventional)</td>
<td>19.5</td>
<td>4</td>
<td>143</td>
</tr>
<tr>
<td>8</td>
<td>Styrene-maleic anhydride copolymer (Conventional)</td>
<td>21.5</td>
<td>5 - 6</td>
<td>193</td>
</tr>
</tbody>
</table>

1. Sizing degree was determined by the Stockigt method (JIS P 8122).
2. Writability was tested by the method of J. Tappi Standard, No. 12.
3. IGT surface strength was determined by the method of J. Tappi Standard T 499 Su-64. Surface strength of Paper (IGT Tester).

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A surface sizing composition for paper, which comprises:
   a copolymer of styrene and at least one unsaturated carboxylic compound selected from the group consisting of maleic acid, maleic anhydride and half esters of maleic acid, wherein said copolymer has a carboxylate equivalent of 80 – 300 based on the free carboxylic acid form, wherein said copolymer has 5 – 50% of its total carboxylic groups as alkali metal salts and 95 – 50% of its total carboxylic groups as at least one non-metal salt selected from the group of ammonium salts and lower alkyl amine salts.

2. The surface sizing composition of claim 1, wherein the molar ratio of styrene to the unsaturated carboxylic compound is 30 – 90: 70 – 10.

3. The surface sizing composition of claim 2, wherein said molar ratio is 45 – 60: 55 – 40.

4. The surface sizing composition of claim 1, wherein the carboxylate equivalent is 100 – 240.

5. The surface sizing composition of claim 1, wherein said copolymer has 10 – 25% of its total carboxylic groups as alkali metal salts and 90 – 75% of its total carboxylic groups as a non-metal salt.

6. The surface sizing composition of claim 1, wherein said half-esters of maleic acid are half-esters of maleic acid with monohydric aliphatic alcohols containing 1 – 20 carbon atoms.

7. The surface sizing composition of claim 1, wherein said alkali metal salt is the sodium salt or potassium salt.

8. The surface sizing composition of claim 1, wherein said non-metal salt is an ammonium salt.

9. The surface sizing composition of claim 1, wherein the lower alkyl ammonium salts are monoalkyl amines, dialkylamines or trialkyl amines which have 1 – 3 carbon atoms in each alkyl group.

10. The surface sizing composition of claim 1, wherein the copolymer has an additional structural unit derived from an ethylenically unsaturated monomer.

11. The surface sizing composition of claim 10, wherein the ethylenically unsaturated monomer is an acrylate or methacrylate having 4 – 12 carbon atoms.

12. The surface sizing composition of claim 1, wherein the free carboxylic acid content of the copolymer is less than 45% of the total carboxylic groups.

13. The surface sizing composition of claim 1, which further comprises a modifier.

14. The surface sizing composition of claim 13, wherein said modifier is a starch, a polyvinyl alcohol, a rosin or a petroleum resin.

* * * *