

1

3,065,041

**METHOD OF GRAFT-POLYMERIZING ACRYLATE MONOMERS ONTO PAPER IN PRESENCE OF ETHYLENE DIMETHACRYLATE, AND RESULTING PRODUCT**

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This invention relates to a novel process for polymerizing certain lower alkyl acrylates with a cellulosic paper in the presence of a polymerizable cross-linking agent and to the products thus produced. Still further, this invention relates to a method for treating cellulosic paper webs by reacting the same with a monomeric lower alkyl acrylate while polymerizing said acrylate and cross-linking the polymerized reaction product with small quantities of a polyfunctional cross-linking agent.

One of the objects of the present invention is to produce an improved cellulosic product by reacting a cellulose containing paper with a monomeric lower alkyl acrylate in the presence of a cross-linking agent. A further object of the present invention is to improve the properties of cellulosic paper webs by practicing the process of the present invention. These and other objects of the present invention will be discussed in greater detail hereinbelow.

In the practice of the process of the present invention, a cellulosic paper is graft polymerized with a lower alkyl acrylate in an aqueous system using a ceric salt as the polymerization initiator and in the presence of small quantities of certain cross-linking agents. The aqueous system may be either a solution of the particular monomer employed in water or a system wherein the monomer is in the aqueous medium in a dispersed and/or emulsified state. These latter systems are preferred.

The cellulosic paper substrates suitable and operable in the process of the present invention can be any one of the well known cellulosic types. This designation is broadly intended to include paper fabricated from natural cellulose fibers and/or regenerated cellulose fibers. One may additionally use paper substrates which contain comparatively small amounts of noncellulosic fibers such as glass, rayon, superpolyamides (polyhexamethylenedipamide), polyacrylonitrile and similar synthetic type fibers. It is preferred that the amount of the noncellulosic fibers of these types does not constitute more than about 20% of the total weight of the paper substrate. It is additionally preferred that the cellulosic paper substrates to be employed in the practice of the process of the present invention be reasonably free of systems other than the fibrous material composing the paper. By other systems, it is meant the various inorganic fillers and water insolubles that may be present in paper. It is not imperative that the paper substrate be free of these materials, but desirably so, from an efficiency standpoint in that the inert materials such as inorganic materials do not contribute significantly to the products of this invention and, of course, if these impurities are water soluble, they are leached out by the aqueous medium and in such instance would serve no useful purpose within the reaction system. Furthermore, it is not imperative that the cellulosic paper substrates employed in the practice of the present invention be of any particular porosity. Nevertheless, the porosity of the paper is important from the standpoint of an efficient processing technique. It has been observed that in the practice of the process of the present invention porous paper allows the monomers and ceric ions to penetrate readily the interstices of the substrate thereby facilitating the grafting mechanism so that a considerable

2

area of the substrate becomes readily available as potential grafting points. Obviously, there are almost unlimited numbers of fabricated papers varying in thickness and degree of porosity which may be used in the practice of this invention. This invention, therefore, contemplates the use of all of these grades of paper to prepare the products of this invention. In carrying out the process of the present invention, the cellulosic substrate is suspended in the aqueous medium containing the ceric ion and the monomeric acrylate with the pH of the system adjusted to 3.5 or below and in the presence of between about 0.01% and 1.0% by weight based on the total weight of monofunctional acrylate of a divinylidene monomeric compound having at least two ethylenic linkages which are in conjugation with other unsaturated linkages which latter are themselves nonethylenic. The cellulosic substrate in the system serves as a backbone onto which the monomeric acrylate is grafted. Upon the addition of the ceric salts, and under the pH conditions required, the graft polymerization reaction begins. Theoretically, at least, each hydroxyl group of the cellulose substrate serves as a potential grafting point. The number of these reactive groups which provide actual graft points is a function of the ceric ion concentration, among other factors, including the particular acidity of the system, the temperature at which the graft polymerization is carried out and the concentration of monomer in the system. Once these grafts are accomplished, the polymeric links to which the monomer extends is a function of monomer concentration, ceric ion concentration, temperature and time of reaction. The amount of pickup, i.e., the amount of polymeric material chemically attached to the substrate may be varied over a fairly wide range. This range can be conveniently expressed in the terms of the original dry weight of the cellulosic paper substrate. Using such a basis, the pickup amounts contemplated herein range from about 100% to about 900% and preferably from about 200% to about 500%.

In carrying out the process of the present invention, the temperature may be controlled between about  $-5^{\circ}$  C. and  $100^{\circ}$  C. but preferably at temperatures between about  $10^{\circ}$  C. and  $60^{\circ}$  C. Temperatures significantly above  $70^{\circ}$  C. are to be avoided because the hydroxyl groups of the cellulosic paper and the ceric salts used herein constitute a redox system which is prone to decompose too rapidly at these elevated temperatures, thus diminishing the effectiveness of the system.

The process of the present invention may be carried out under superatmospheric pressure or even under partial vacuum but it is preferred for practical purposes to utilize atmospheric pressure inasmuch as the reaction runs very favorably at this pressure.

The graft polymerization reaction of the present invention is carried out in an acidic aqueous medium. The pH of said medium may be any value up to and including 3.5. For optimum results, it is preferred that the pH value be maintained between 1 and 2. Suitable acids for obtaining the desired pH are adequately shown in the specific examples set forth hereinbelow.

The amount of ceric compound which is utilized in the practice of the process of the present invention may be varied over fairly wide limits. For example, one may utilize from about  $10^{-6}$  to  $10^{-1}$  mol of ceric ion per mol of polymerizable monomer. Preferably, one would use between  $10^{-3}$  to  $10^{-2}$  mol of ceric ion per mol of polymerizable monomer. Ceric ion is preferably introduced into the reaction mixture according to the present invention in the form of a ceric salt. Among the salts adapted for use in the present invention are ceric nitrate, ceric sulfate, ceric ammonium nitrate, ceric ammonium sulfate, ceric ammonium pyrophosphate, ceric iodate and

the like. These compounds may be employed singly or in combination with one another. Ceric compounds which are capable of forming ceric salts in situ under the acid conditions of the polymerization reaction such as ceric oxide, ceric hydroxide and the like may be used.

The monomers useful in preparing the novel products of this invention are certain alkyl esters of acrylic acid. Specifically, these monomers are ethyl acrylate, propyl acrylate, and butyl acrylate. The various isomeric forms of propyl acrylate and butyl acrylate, namely, isopropyl acrylate, sec-butyl acrylate, tert-butyl acrylate are contemplated herein. Obviously, these monomers may be used singly or in combination. All of the monomeric substances mentioned hereinabove give types of plastic products having the singular properties attributed to the products of this invention.

The cross-linking agents used in the practice of the process of the present invention should be present in amounts varying between about 0.01% and 1% by weight of a polymerizable compound containing at least two polymerizable  $\text{CH}_2=\text{C}<$  groups. These vinylidene monomeric compounds must have at least two ethylenic linkages which are in conjugation with other unsaturated linkages which later unsaturated linkages are themselves nonethylenic. Among the cross-linking agents of this class which may be used in the practice of the process of the present invention are such monomers that result from the full esterification of a glycol with an alpha, beta-ethylenically unsaturated monocarboxylic acid. More particularly, these cross-linking agents result from the complete esterification of ethylene glycol, propanediol-1,3, butanediol-1,4 and the like, with acrylic acid, methacrylic acid and the like. As specific compounds, one may use ethylene diacrylate, propylene diacrylate, butylene diacrylate, ethylene dimethacrylate, propylene dimethacrylate, butylene dimethacrylate and the like. In addition, one may use such cross-linking agents as divinyl benzene, divinyl naphthalene and the like. The alkylene bis acrylamides may also be utilized effectively such as those disclosed in the U.S. Patent No. 2,475,846. Obviously, these cross-linking agents may be used either singly or in combination with one another.

It has been indicated hereinabove that the process of the present invention can be carried out in aqueous solution but preferably in a dispersion or an emulsion medium. In the latter instance, advantageous use of an emulsifying agent can be made of which agents a substantial plurality are well known in the art and the technique for using the same has been so widely published that further description herein is deemed to be unnecessary.

In order that the concept of the present invention may be more fully understood, the following examples are set forth in which all parts are parts by weight unless otherwise indicated. These examples are set forth primarily for the purpose of illustration and any specific enumeration of detail contained therein should not be interpreted as a limitation on the case except as is indicated in the appended claims.

#### Example 1

An emulsion is prepared by mixing, in a Waring Blendor for 3 minutes, 2250 parts of distilled water, 125 parts of a mixture of monomeric n-butyl acrylate and ethylene dimethacrylate (99.9%–0.1% respectively, each inhibitor free) and 1.425 parts of octadecyl trimethyl ammonium chloride, 50% solids in water. The emulsion thus prepared is introduced into a suitable reaction vessel equipped with a purging tube. 12.5 parts of a cellulosic filter paper is immersed in the emulsion. The system is purged for 30 minutes with prepurified nitrogen at 500 parts per minute whereupon 125 parts of a 0.1 molar solution of ceric ammonium nitrate in 1 molar nitric acid is added and the purging continued during the entire run. After reacting at 25° C., the treated paper is removed and washed thoroughly with water. The paper is dried to a

constant weight at 220° F. and the paper shows a polymer pickup of 100 parts per hundred parts of paper weight.

#### Example 2

Example 1 is repeated in all details except that the reaction time is increased to give a polymer pickup of 250 parts per hundred parts of paper weight.

#### Example 3

Example 1 is repeated in every detail except that the weight ratio of the monomeric n-butyl acrylate to the ethylene dimethacrylate is 99%–1%, respectively.

#### Example 4

Example 2 is repeated in every detail except that the weight ratio of the monomeric n-butyl acrylate to the ethylene dimethacrylate is 99%–1%, respectively.

#### Example 5

Example 1 is repeated in every detail except that no cross-linking agent is used with the n-butyl acrylate.

#### Example 6

Example 2 is repeated in every detail except that no cross-linking agent is used with the n-butyl acrylate.

#### Example 7

Example 1 is repeated in all details except that the monomer to cross-linking agent was 99.5%–0.5%, respectively.

#### Example 8

Example 2 is repeated in all details except that the monomer to cross-linking agent was 99.5%–0.5%, respectively.

The results realized are set forth in Table I hereinbelow.

TABLE I

Example	Pick-up of Polymer Grafted, phr.	Dry Burst Strength, p.s.i.
Control		15.7
1	100	31
2	250	52
3	100	28
4	250	45
5	100	22
6	250	33
7	100	31
8	250	54

1. A process comprising graft polymerizing a monomeric compound selected from the group consisting of ethyl acrylate, propyl acrylate and butyl acrylate in the presence of from about 0.01% to about 1% by weight, based on the total weight of said acrylates, of ethylene dimethacrylate onto a paper substrate composed predominantly of cellulosic fibers in an aqueous medium at a pH not greater than 3.5 in the presence of a ceric salt which is soluble in at least one component of the reaction medium until the weight of said monoacrylate grafted onto said substrate is between 100% and 900% based on the weight of the substrate.

2. A process comprising graft polymerizing butyl acrylate in the presence of from about 0.01% to about 1% by weight, based on the weight of said acrylate of ethylene dimethacrylate onto a cellulosic paper web composed predominantly of cellulosic fibers in an aqueous medium at a pH not greater than 3.5 in the presence of a ceric salt which is soluble in at least one component of the reaction medium until the weight of said butyl acrylate grafted onto said substrate is between 100% and 900% based on the weight of the substrate.

3. A process comprising graft polymerizing ethyl acrylate in the presence of from about 0.01% to about 1% by weight, based on the weight of said acrylate of ethylene dimethacrylate onto a cellulosic paper web com-

5

posed predominately of cellulosic fibers in an aqueous medium at a pH not greater than 3.5 in the presence of a ceric salt which is soluble in at least one component of the reaction medium until the weight of said ethyl acrylate grafted onto said substrate is between 100% and 900% based on the weight of the substrate.

4. A process comprising graft polymerizing propyl acrylate in the presence of from about 0.01% to about 1% by weight, based on the weight of said acrylate of ethylene dimethacrylate onto a cellulosic paper web composed predominately of cellulosic fibers in an aqueous medium at a pH not greater than 3.5 in the presence of a ceric salt which is soluble in at least one component of the reaction medium until the weight of said propyl acrylate grafted onto said substrate is between 100% and 900% based on the weight of the substrate.

5. A cellulosic paper web reacted with butyl acrylate and from about 0.01% to about 1% by weight, based on the weight of said acrylate of ethylene dimethacrylate, wherein said butyl acrylate on said paper is in a graft-polymerized state and is present in an amount varying between about 100% and 900% by weight based on the weight of said paper web.

6. A cellulosic paper web reacted with propyl acrylate

6

and from about 0.01% to about 1% by weight, based on the weight of said acrylate of ethylene dimethacrylate, wherein said propyl acrylate on said paper is in a graft-polymerized state and is present in an amount varying between about 100% and 900% by weight based on the weight of said paper web.

7. A cellulosic paper web reacted with ethyl acrylate and from about 0.01% to about 1% by weight, based on the weight of said acrylate of ethylene dimethacrylate, wherein said ethyl acrylate on said paper is in a graft-polymerized state and is present in an amount varying between about 100% and 900% by weight based on the weight of said paper web.

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