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(57) Abstract

Acrylic copolymer compositions which contain a tackifying hydrocarbon resin and the use of such composition in pressure sensitive adhesives are described. The tackifying hydrocarbon resin is dissolved in a solution of alkyl (meth) acrylate and (meth) acrylic acid monomers and is present during the polymerization of the monomers to form a tackified acrylic copolymer.

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INTERNAL RESIN - TACKIFIED ACRYLIC POLYMER

This invention relates to acrylic copolymer latex compositions which contain a tackifying hydrocarbon resin and the use of such composition in pressure sensitive adhesives. The tackifying hydrocarbon resin is dissolved in acrylic monomers to form a homogeneous solution and is present during emulsion polymerization of the monomers to form the acrylic copolymer latex.

<u>Background of the Invention</u>

Tackified acrylic copolymers are used as pressure sensitive adhesives. Such tackified copolymers have usually been prepared by physically mixing a tackifying petroleum-based hydrocarbon resin, or a natural resin with a polymerized acrylic copolymer. While the resulting adhesive is often satisfactory to obtain certain properties such as tackiness and peel strength on substrates such as polyester or stainless steel, certain properties are found to be deficient, particularly the holding power on these same substrates. Previously, increasing the peel strength of tackified acrylic copolymers to a value greater than 2.0 pounds per inch caused the holding power (1 Kg over one inch square on stainless steel) to diminish to below 40 hours. Of course, it is desirable to maintain high holding power, particularly when the pressure sensitive adhesive is to be used to prepare an adhesive tape.

The prior art describes attempts to prepare satisfactory tackified acrylic copolymers. For example, Japanese Patent J-59213783 teaches the preparation of a hot-melt pressure sensitive adhesive by first heating a tackifying resin having a softening point between 60 and 200°C to above its melting point, and adding to the hot melt a polymerization mixture of alkyl (meth) acrylate, a functional monomer such as acrylic acid, and a free radical initiator. The polymerization mixture is added to the hot melt over a period of several hours, with stirring, to form a pale yellow, transparent solid hot-melt adhesive. The tackifying resins are broadly identified to include rosin-based resins, terpene-phenol-resins, phenol resins, coumarone resins, aliphatic and aromatic resins.

Japanese Patent J-59227967 discloses a hot-melt polymerization of an alkyl (meth) acrylate monomer and a functional comonomer including (meth) acrylic acid, maleic anhydride, maleic acid, vinyl ethers, and the like, where a surfactant is present with the resin during the polymerization to form a solid mass, hot-melt adhesive. In Japanese Patent 53074041 a polymerized powdery toner product is obtained by dissolving a binder resin such as a vinyl resin, acetal resin, epoxy resin, or the like, in a polymerizable liquid monomer such as styrene, vinyl toluene, (meth) acrylic acid or its ester and the like, and polymerizing the monomers in bulk in the presence of a coloring material.

In Japanese Patent J-51125472, a petroleum resin emulsion is obtained by polymerizing vinyl monomers in the presence of petroleum resins having softening points of from 40 to 160°C, an average molecular weight of 300 to 3000, and an acid value and saponification value of less than 1. The monomers include, for example, alkyl (meth) acrylates, vinyl acetates and vinyl chlorides, styrene, acrylonitrile, and acrylic acid. The emulsified mixture is then reacted in an emulsion polymerization reaction to form a shelf-stable emulsion adhesive. The resin emulsion produced is described as having fine particle sizes and ample stability, and, when cured, the films produced have excellent water resistance and gloss. Also, U. S. Patent 4,645,711 specifically describes the incorporation of hydrocarbon resins from many sources, i.e., from hydrogenated resin esters, polyterpene, polymerized alkyl styrene, and polymerized petroleum-derived monomer resins, into pressure sensitive adhesive tape compositions where the adhesive is a polymerized acrylic emulsion. The patent describes physically mixing the resin with the polymer emulsion rather than dissolving the resin in the monomer, forming the emulsion and then polymerizing the monomers.

Numerous approaches have been used to produce resin emulsions. One approach is to dissolve the resin in a hydrocarbon solvent, combine the resin solution and water to form an emulsion, and strip the solvent. Invariably some residual hydrocarbon solvent remains in the finished emulsion, which is undesirable in certain applications. This has led to the development of solvent-free dispersions (see U. S. Patent No. 2,809,948) and emulsions (see U. S. Patent No. 3,377,298) of petroleum resins. In both of these formulations, ionic emulsifiers have been utilized; in the former a mixture of cationic and non-ionic surface active agents is used to achieve a resin emulsion; and, in the latter an ionic surfactant is used in combination with an aqueous gel of a swelling earth to produce an emulsion paste of a petroleum resin. These resin emulsions have been commercially used to tackify natural rubber, carboxylated styrene-butadiene and acrylic latexes for many adhesive applications.

As mentioned above, there has generally been a decrease in shear properties associated with an increase of peel strength and tackiness. There is a need to improve the peel strength of pressure sensitive adhesives while yet maintaining high shear properties and thus obviating the decline in shear usually resulting from increase in peel.

Accordingly, it is an object of this invention to prepare a resin-tackified acrylic copolymer in the form of a latex-like dispersion for application as pressure sensitive adhesives having increased peel strength without serious decrease in shear.

It is a further object to provide a process for preparing a resin-tackified acrylic copolymer, wherein the tackifying resin is dissolved in the acrylic monomer solution prior to the polymerization reaction.

It is a still further object of this invention to provide pressure-sensitive adhesives useful to prepare tapes and useful laminating adhesives.

<u>Summary of the Invention</u>

A tackified acrylic copolymer is prepared by dissolving a hydrogenated natural resin or petroleum hydrocarbon resin in a liquid monomer mixture from which the copolymer is to be prepared by free radical initiated emulsion polymerization. The resin, having an aromatic content of at least about 10 wt.%, is present in amounts of from about 10 to about 100 parts by weight preferably 20 to 60 parts, per 100 parts of the acrylic monomers. The resin is dissolved in the monomers at ambient temperatures or higher, and the free-radical polymerization reaction is conducted, with stirring, at a temperature from about 25°C to about 90°C.

A dispersion of polymer in the form of a latex is produced which may be easily coated over a substrate, such as flexible polyester or polyolefin films, where it is dried to form a pressure sensitive adhesive having a good balance of peel strength and shear strength.

Detailed Description of the Invention

Resins useful in the present invention are generally well known and are defined as hydrogenated natural resins and thermoplastic petroleum hydrocarbon resins obtained by polymerization, in the presence of a catalyst of the Friedel-Crafts type, of steam-cracked petroleum distillates, boiling in the range between about 30°C and 280°C, or any fraction of these distillates boiling within the said range, or of polymerized mixtures of olefins and diolefins.

The hydrocarbon resins useful according to this invention are preferably petroleum resins prepared by homo and copolymerization of olefins, diolefins, and vinyl aromatic components, predominantly the C_5 to C_9 species, from distillates of cracked petroleum stocks. The feedstocks for the resin must, however, have at least about 10% by weight vinyl aromatic constituents, such as, for example, styrenes, alpha-methyl styrene, indene and vinyl toluene and other well known vinyl aromatic compounds. A Friedel-Crafts catalyst is typically employed and this resin-forming polymerization is performed at temperatures which range generally from 0° to 70°C and preferably from 30°C to 55°C. The resulting resin is then hydrogenated in accordance with the methods described in U. S. Patent Nos. 4,650,829; 4,328,090 and 4,629,766, for example, the disclosures of which are incorporated herein by reference in their entirety for all purposes. The resulting hydrogenated resin retains a ring and ball softening point in the range of -20°C to about 150°C, preferably from about 10°C to about 100°C. In the practice of this invention the pressure sensitive adhesives formed from resins having a softening point from 15°C to about 40°C typically find their best use as laminating adhesives or adhesives for labels, those having softening points from about 70°C to 100°C for tapes.

Broadly, hydrocarbon resins are polymerized from petroleum cracked distillates boiling in the range of about 30°C to 280°C or any fraction boiling within this range having a vinyl aromatic content as set forth above. As is well known, the resins are prepared by treating the distillate with from 0.25 to 2.5% by weight of a Friedel-Crafts-type catalyst such as aluminum chloride, aluminum bromide, boron trifluoride, and the like, or solutions, slurries, or complexes thereof. The reactions are conducted at temperatures in the range of 0° to 70°C, and preferably 30°C to 55°C. Residual catalyst is quenched by suitable methods such as addition of methyl alcohol and subsequent filtration, water, and/or caustic washing. The final solution is then stripped of unreacted hydrocarbons and low molecular weight oils by vacuum or steam distillation. Properties of the hydrocarbon resins can be varied by changing conditions and feedstock as is well known.

The hydrocarbon resin is prepared by the hydrogenation of polymerized olefinically unsaturated monomers derived from petroleum cracking, preferably cyclic diolefin, such as, for example, dicyclopentadiene, styrene, alpha-methylstyrene and the like. Such resins, their preparation and hydrogenation are well known in the art and are commercially available under the trade designations, for example, Escorez, Arcon and the like.

Naturally occurring resins suitable for use in the present invention may be resin esters or terpenes such as alpha-pinene, beta-pinene, carene, limonene or other readily available terpinous materials, alpha-pinene and limonene being preferred. The material may be pure or the commercially available concentrates such as gum terpentine or alpha-pinene concentrates, which tend to be mixtures of various terpinous materials. A suitable natural resin contains from about 70 to 95 wt.% alpha-pinene, the remainder being other terpenes. Limonene and carene streams are available and are known to those in the art. These are typical streams useful in the present invention. The hydrogenation of these naturally occurring resins is well known and can be carried out using the procedures of the above-identified U. S. patent.

It has been discovered in the practice of this invention that the most successful tackified acrylic copolymers are produced when the resin is readily soluble in the selected monomer mixture at ambient temperature. Such resin should have a molecular weight of from about 500 to about 5000 and, preferably from about 1500 to about 2500.

When the aromatic contents of the resin, usually a styrene or a vinyl toluene or vinyl xylene derivatives, decrease below about 30 wt.%, the mixture of acrylic monomers must be adjusted to reduce overall polarity of the monomer mixture in a manner well known to those skilled in such polymerizations. For example, a substitution of butyl acrylate for 2-ethylhexyl acrylate would reduce polarity. By lowering the polarity of the monomer mixture, lower aromaticity in the resin can be tolerated and the resin will still dissolve in the monomers to form a solution.

It has further been discovered that aliphatic resins, such as those formed from amylenes, piperylene, cyclopentadiene and its derivatives are not necessarily soluble in the monomers selected, and thus are normally not desirable. In accordance with this invention, as previously mentioned, in order to form a suitable polymerization reaction mixture, it is necessary that the resins comprise from at least 10% to 100% by weight vinyl aromatic content, preferably from about 20% to about 65% aromatic content with 30% to 50% being a most preferred range.

The monomers used in the practice of this invention are those which are polymerizable by free radical reactions, preferably those materials generally described as acrylics; i.e., alkyl (meth) acrylates and (meth) acrylic acid. Mixtures of alkyl acrylates are usually included, which affect the solubility of the petroleum resins prior to polymerization as well as final properties of the copolymer composition. These acrylate monomer mixtures generally comprise lower alkyl (meth) acrylates having 1 to 3 carbon atoms in the alkyl group of the ester and upper alkyl (meth) acrylates having four or more, usually up to about 14, carbon atoms, but preferably from five to about eight carbon atoms. The other monomer component is the (meth) acrylic acid. Some preferred examples of monomers are as follows: acrylic acid, (meth) acrylic acid, crotonic acid, maleic acid, itaconic acid, methyl (meth) acrylate, ethyl (meth) acrylate, propyl acrylate, 2-ethylhexyl acrylate, n-butyl acrylate. Other monomers which can be employed include acrylnitrile, vinyl acetate, vinylidene chloride, styrene, methyl styrene, and the like. The monomer mixture should contain from 1% to about 15%, preferably about 2% to about 6% of the (meth) acrylic acid; 0 to about 50%, preferably about 10% to 35%, lower alkyl (meth) acrylate; and from about 25% to 99%, preferably from 60% to about 88% upper alkyl (meth) acrylate. All percents are by weight of the monomer mixture. It should be noted that some "acrylic" monomer mixtures available include minor amounts of acrylonitrile, styrene, or vinyl acetate, and the like.

Generally the reaction of acrylic monomers to form acrylic copolymers is well known to those practitioners in the art to include water to adjust the solids content, a surfactant to aid in the formation of monomer-in-water emulsion and to act as a suspending agent for the solids in the final copolymer, which are dispersed in the aqueous medium both during and after the polymerization. The surfactants useful in the practice of this invention are well known and are present in quantities sufficient to place the reactants in the emulsion prior to reaction and maintain the product in suspension after the reaction. Of particular applicability are a blend of anionic and nonionic surfactants having a HLB of from about 15 to 42, especially from about 35 to about 40. Especially preferred is the widely used disodium sulfosuccinate as an ionic surfactant and ethylene oxide adducts of nonyl phenol as nonionic surfactants. While the ranges of surfactants are well known, the amount will preferably range from about 1 to about 5 parts, normally 2 to 4 parts per 100 parts of the monomers. Also present in the reaction mixture is an initiator, such as for example, sodium persulfate or an ammonium persulfate present in amounts well known to those skilled in the art, such as for example, about 0.1 part per 100 parts of monomer in the reaction mixture. In some instances it may be advantageous to buffer the pH of the solution by including some well known buffering agent such as, for example, sodium bicarbonate.

Notwithstanding the foregoing, the selected petroleum or natural resin is dissolved into the selected monomers to form a solution containing from about 10 to about 100 parts resin per 100 parts of the liquid mixture of monomer reactants and more preferably from about 20 to about 60 parts per 100 parts of monomer reactants. Most preferably, from 25 to 55 parts resin per 100 parts of monomer reactants are present. As stated hereinbefore, the resin is selected so that it will be readily soluble in the monomer mixture at ambient temperatures, but notwithstanding such, the temperature could be raised to the point where it is easily solubilized, i.e., from about 25°C to about 40°C.

The molecular weight of such copolymers is normally controlled by commonly known nonolefin chain transfer agent in the polymerization mixture. In the practice of the present invention, the copolymer is to be formed with no chain transfer agent being used which restricts the molecular weight of the copolymer. Similarly, we have discovered that the presence of an antioxidant in the resin is to be avoided because it causes the same problem--low molecular weight of the polymer. It is preferred that the solution of monomers and resin be dispersed into a water medium to form an emulsion at ambient temperatures with only stirring in the presence of a satisfactory surfactant. The reaction mixture thus formed, including the initiators, must be placed in a reaction vessel, evacuated of oxygen, by purging with nitrogen, and the polymerization reaction conducted with stirring in the sealed container under a nitrogen blanket.

The addition of the monomer solution containing the hydrocarbon resin is normally carried out intermittently and over a period of time. For example, about 15 wt.% of the monomer solution is initially metered into the reaction mixture and polymerized for a short period of time. Normally, when this is accomplished, the solids content of the reaction would be about 18 wt.%, which is preferably a benchmark content. Once the selected solids level is attained, the balance of the monomer solution is evenly metered into the reaction vessel over a period of time, usually 3 to 6 hours, depending upon the size of the reactor and quantity to be added. Once the addition of the monomer mixture is complete, the polymerization is allowed to continue, usually for about another hour while maintaining the reaction temperature, normally, within the range of from about 45°C to about 90°C, preferably between about 50°C and 80°C. The polymerization continues until the total solids content of the material in the reactor reaches its theoretical level based upon the amount of reactants charged to the reaction mixture, usually in practice, about 45 to about 55 weight percent but the overall solids content may be as high as 70% with there being no real lower limit. While there is no real theoretical lower limit, a practical lower limit of about 30% solids content is recognized by those skilled in the art. In a commercial sense the highest limits attainable are preferred.

Once the reaction is complete, the solids, in the form of a dispersed polymer latex, is allowed to cool to room temperature, and the dispersed polymer latex is separated from coagulum formed during polymerization, usually by filtration. In the practice of this invention, a 200 mesh "sock" filter has been found satisfactory. Such latex can be coated on a substrate film for use as a tape, for example. The coated substrate would be dried, usually by circulating hot air at from about 100°C to about 110°C for a few, usually from about 2 to about 5, minutes. Those skilled in the art would readily recognize other processing parameters for such coated substrate. The latex coating usually results in a dried adhesive film of from about 0.5 to about 1.5 mils, preferably about 1.0 mil of thickness, even though thicker or thinner films may be desired in certain applications of the instant invention. Thus dried and cured, the product is in condition for use as pressure sensitive adhesives.

In certain embodiments of the practice of this invention, the adhesives formed find applications as non-pressure sensitive adhesives such as, for example, laminating adhesives, binders for woven and nonwoven fabrics and binders for pressed wood production. For example, the certain species useful as laminating adhesives, i.e., those with high peel strength but low shear properties, would be used to join two or more sheets of material together such as joining a layer of wood or a multiple layer of wood to form a plywood product.

The foregoing invention having now been described, the following examples are to further teach the preferred embodiment and best modes for practicing the described invention and to aid others in the practice of the scope of such invention herein provided.

Example 1 - Comparative

This example illustrates the synthesis of acrylic copolymer emulsions. The actual ingredients charged into the reactor are summarized in Table 1 below. Various amounts of the chain transfer agent, t-dodecanethiol are used in the preparation of Samples 1-4, in order to obtain the copolymers with various molecular weight.

Table 1

A. Initial Charge:

24.0 parts distilled water
0.1 parts Igepal CO-850, an ethylene oxide adduct of nonyl phenol (sold by GAF)
0.2 parts sodium bicarbonate
0.05 parts sodium persulfate

B. Monomer Mixture:

24.2 parts distilled water
3.16 parts Emcol K-8300, an anionic surfactant manufactured by Witco Chemical
0.05 parts sodium persulfate
37.5 parts 2-ethylhexyl acrylate
10.5 parts ethyl acrylate
2.0 parts acrylic acid
0-0.1 part t-dodecanethiol

A 2-liter, four-neck reaction flask equipped with a stirrer, a condenser, a thermosensor, and a monomer addition tube was flushed with nitrogen for 15 minutes. The initial charge (A) was placed in the flask with stirring and continued nitrogen purging for additional 20 minutes. At the end of the 20 minutes, the temperature was raised to 65°C.

In a separate vessel, a monomer mixture according to the composition (B) was prepared. When the reaction flask temperature was equilibrated at 65°C, 15 wt.% of the monomer mixture (B) was charged to the flask and allowed to polymerize for 30 minutes. The total solids at the end of the 30 minutes should be 15-17%. When the total solids reached this range, the remaining monomer mixture (B) was evenly metered into the flask over a period of 3 hours. After the monomer addition, the reaction was allowed to continue at 65°C for 2 additional hours and then cooled to room temperature. Stirring was continuous throughout the procedures.

The final total solids was about 50% by weight, particle size, 150-250 nm, and Brookfield viscosity, 500-1000 cp. The coagulum content of about 2% of the total reactants charged was removed by filtration.

Pressure Sensitive Adhesive (PSA) Performance Test

The polymer latex prepared as described above was knife-coated on a Mylar® film and dried in an air circulating oven for 3 minutes at 110°C. The dried adhesive coating was approximately 1.5 mils thick. The adhesive was bonded to a stainless steel surface for PSA performance tests. Peel (180°C) adhesion was obtained using Test No. PSTC-1 of the Pressure Sensitive Tape Council. Shear test was performed using PSTC-7. SAFT test was similar to shear test except that the test temperature is increased at the rate of 10°F per 15 minutes. The temperature at which shear failed is reported as SAFT. Both SAFT and shear were tested at 1 square inch and 1000 gram hang weight.

PSA performance is very sensitive to the molecular weight of the polymer. A chain transfer agent such as t-dodecanethiol is commonly used to control the molecular weight and to demonstrate the sensitivity. Table 2, below, summarizes the PSA test results for Samples 1-4 which were synthesized according to the above procedures, but with varying amounts of chain transfer agent.

Table 2

Samples	Dodecanethiol (parts)	180° Peel (lbs/in)	SAFT (°F)	Shear (hrs)
1	0.0	1.1	290+	100+
2	0.025	1.1	290+	100+
3	0.05	1.6	290+	18
4	0.075	1.7	112	3

Samples with t-dodecanethiol level higher than 0.075 parts show cohesion failure in the peel test and have very poor shear, less than 1 hour. These samples are not useful for PSAs.

Example 2 (Comparative)

The sample #1 from Table 2 was mixed with 20 to 100 parts of resin emulsion ECR-109A (Exxon Chemical Company, Houston, Texas) per 100 parts of an acrylic copolymer emulsion. The resin emulsion ECR-109A is made by direct emulsification of the hydrocarbon resin and contains 55% total solids. The PSA performance results of the acrylic emulsion and resin emulsion blend are summarized in Table 3 below.

Table 3

Samples	Level (PHR)	180° Peel (lbs/in)	SAFT (°F)	Shear (hrs)
5	0	1.1	290+	100+
6	20	1.6	290+	88
7	50	2.2	290+	36
8	100	2.6	221	18

Example 3

The synthesis procedures described in Example 1 were followed using initial charge and monomer emulsion compositions of Table 1, except that the monomer composition for the Samples 5-8 were changed to include different amounts of petroleum resins (ESCOREZ ECR-149, MW-1000, 50 wt.% aromatics--Exxon Chemical Company, Houston, Texas) dissolved in the monomer solution as illustrated in Table 4 below (all ingredient units are in parts) by weight. No chain transfer agent was used. ECR-149 has an average molecular weight of about 1000, 50 wt.% aromaticity and similar structure and softening point to the starting resin emulsion ECR-109A. It is obtained by the hydrogenation of the starting resin of ECR-109-A.

Table 4

Samples	ECR-149	Acrylic Acid	Ethyl Acrylate	2-Ethylhexyl Acrylate
9	10.0	1.6	8.4	30.0
10	11.6	2.3	7.7	28.4
11	11.6	1.5	8.1	28.8
12	15.0	1.4	7.4	26.2

The PSA performance results of above samples obtained following same produces and at same conditions are summarized on Table 5 below.

Table 5

Samples	180° Peel (lbs/in)	SAFT (°F)	Shear (hrs)
9	1.6	290+	100+
10	2.4	290+	100+
11	2.5	290+	26
12	3.1	188	22

Comparing the results in Table 4 with Table 2, it is clear that a significantly higher peel strength PSA product can be developed while maintaining high shear properties. The improved balance of peel and shear properties cannot be obtained through conventional acrylic composition using externally introduced tackifier as shown in Example 2.

Example 4

To demonstrate the applicability of this invention to a wide range of hydrogenated resins having greater than 10% by wt. aromaticity and a wide range of softening points, the procedures of Examples 1 and 3, including PSA performance, were followed. The results of these experiments are shown on Table 6.

Table 6

Sample Number	Resin Used (ECR#**)	Softening Point, °C	Resin Level, PHR	PSA Performance Peel (lbs/in)	SAFT (°F)	Shear (hrs.)
13	-	-	0	1.1	290+	100+
14	424-36	36.6	40	5.2*	105	1.9
15	424-37	19.5	40	4.1*	104	1.3
16	149-1D	90.5	30	2.3	300+	37
17	149-1D	90.5	40	2.6	253	100+
18	149-1D	90.5	50	2.8	244	100+
19	149-BPC	87	30	2.8	266	100+
20	149-BPC	87	40	2.7	136	71
21	149-BPC	87	50	3.3	128	40
22	149-BPC	87	50	2.5	253	100+
23	149	95	25	1.6	290+	100+
24	149	95	30	2.7	300+	26
25	149	95	40	3.1	188	22
26	Foral***	104	40	2.1		0.4
27	Staybelite Ester 10	83	40	5.4*		0.3

* Cohesive failure.

** ESCOREZ Resins (Exxon Chemical Company).

Aromaticity, wt.%: ECR 424-30% ECR 149 = 50%.

*** Foral 105-P (Hercules Chemical Company) - contains antioxidant.

Stabelite ester 10 is the Glyceral ester of hydrogenated resins (Hercules) - contains antoxidant.

As seen by the foregoing Table 6, resins having softening points from about 19.5°C to about 104°C can be used in the practice of this invention. As a general consideration, resins having softening points between 70 and 100°C are especially adaptable for use with tapes while those in the 15 to 40 range are considered preferable for labels. For instance, the PSA performance of samples 14 and 15 indicates that they would be good products for use as labels. Samples 26 and 27 though having high softening points, still result in low shear strength due to the minor amount of antioxidants present in the commercial resin product used. The presence of the antioxidant lowers the molecular weight of the finished products and results in weak shear strength. While not adequate for use as a pressure sensitive adhesive for a tape, it would make an adequate laminating adhesive or label adhesive.

Note also from Table 6 that some resins exhibit changes in PSA performance with varying of the resin level. Thus, this example is a guide for those practicing this invention to achieve desired performance levels. Compare also Samples 21 and 22 which are the same product except that Sample 22 has been aged for three months. The shear property improved! With certain resins shear increases with resin level (Samples 16 and 17, for example) and with others it decreases (Samples 19, 20, and 21, for example). Note the effect of resin level demonstrated in Samples 23, 24 and 25 as practiced within the scope of the invention.

As is apparent from the foregoing description, the materials prepared and the procedures followed relate to specific embodiments of the broad invention. It is apparent from the foregoing general description and the specific embodiments that, while predictive forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of this invention. Accordingly, it is not intended that the invention be limited except by the appended claims.

CLAIMS:

1. A tackified acrylic copolymer latex composition comprising:

a hydrogenated hydrocarbon resin, having a molecular weight of from about 500 to about 5000 and an aromatic content of at least 10% by weight; and

an acrylic copolymer formed by free radical initiated polymerization of a monomer mixture comprising alkyl (meth) acrylate and (meth) acrylic acid monomers, having dissolved therein from about 10 to about 100 parts of the polymerizable monomers.

2. The tackified acrylic copolymer latex of Claim 1 wherein the hydrogenated hydrocarbon resin is a natural resin or terpene.

3. The tackified acrylic copolymer latex of Claim 1 wherein the hydrogenated hydrocarbon resin is a petroleum hydrocarbon resin having a softening point of from about -20°C to about 150°C.

4. The tackified acrylic copolymer latex of Claim 1 wherein the monomer polymerized comprises from 1 to about 15 wt.% of a (meth) acrylic acid, 0 to about 50 wt.% of a lower alkyl (meth) acrylate ester and from about 25 wt.% to 99 wt.% of an upper alkyl (meth) acrylate ester.

5. The tackified acrylic copolymer latex of Claim 4 wherein the monomer comprises from 2% to about 6% of a (meth) acrylic acid, from about 10 wt.% to about 35 wt.% of a lower alkyl (meth) acrylate acid, from about 60 wt.% to about 88 wt.% of an upper alkyl (meth) acrylate.

6. The tackified acrylic copolymer latex of Claim 1 wherein the resin is a hydrogenated petroleum hydrocarbon resin having an average molecular weight of from about 500 to about 5000 and an aromatic content of from about 20 wt.% to about 65 wt.% and the monomers include 2 wt.% to 6 wt.% acrylic acid, 10 wt.% to 35 wt.% ethyl acrylate and 60 wt.% to 88 wt.% 2-ethylhexyl acrylate, wherein the resin is present in the polymerization solution in amounts of from 20 to about 60 parts resin per 100 parts monomer.

7. The tackified acrylic copolymer latex of Claim 1 wherein the acrylic copolymer also includes one or more of acrylonitrile, vinyl acetate, vinylidene chloride, styrene and methyl styrene.

8. A method for preparing a tackified acrylic copolymer latex composition which comprises the stem of:

dissolving from about 10 to about 100 parts of a hydrogenated hydrocarbon resin per 100 parts in a liquid mixture of free-radical polymerizable monomers to form a polymerizable vinyl monomer reactant solution, the hydrocarbon resin having an average molecular weight of from about 500 to about 5000 and an aromatic content of at least about 10% by weight;

emulsifying the reactant solution in an aqueous medium;

polymerizing the emulsified monomers, in the absence of oxygen, in the presence of the resin and a free radical polymerization initiator to form an acrylic copolymer latex, and

recovering the tackified acrylic copolymer latex internally tackified by the resin.

9. The method of Claim 8 wherein the hydrogenated hydrocarbon resin is a natural resin or terpene.

10. The method of Claim 8 wherein the hydrogenated hydrocarbon resin is a petroleum hydrocarbon resin having a softening point of of from about -20°C to about 150°C.

11. The method of Claim 8 wherein the monomer polymerized comprises from 1 wt.% to about 15 wt.% of a (meth) acrylic acid, 0 to about 50 wt.% of a lower alkyl (meth) acrylate ester and from about 25 wt.% to 99 wt.% of an upper alkyl (meth) acrylate ester.

12. The method of Claim 11 wherein the monomer comprises from 2% to about 6% of a (meth) acrylic acid, from about 10 wt.% to about 35 wt.% of a lower alkyl (meth) acrylate acid, from about 60 wt.% to about 88 wt.% of an upper alkyl (meth) acrylate.

13. The method of Claim 8 wherein the resin is a hydrogenated petroleum hydrocarbon resin having an average molecular weight of from about 500 to about 5000 and an aromatic content of from about 20 wt.% to about 65 wt.% and the monomers include 2 wt.% to 6 wt.% acrylic acid, 10 wt.% to 35 wt.% ethyl acrylate and 60 wt.% to 88 wt.% 2-ethylhexyl acrylate, wherein, the resin is present in the polymerization solution in amounts of from 25 to about 55 parts per 100 parts monomer polymerized.

14. A polymerizable monomer mixture for preparing an internally resin-tackified acrylic polymer comprising a liquid acrylic vinyl monomer solution comprising a mixture lower alkyl (meth) acrylates, upper alkyl (meth) acrylates, and a (meth) acrylic acid, and

a hydrogenated resin in solution with the vinyl monomer as a solvent wherein the resin has a molecular weight of from 500 to about 5000 and an aromaticity of at least 10% by weight and is present in amounts of from 10 parts to 100 parts resin per 100 parts of vinyl monomer solution.

15. A polymerizable monomer mixture wherein the liquid acrylic also includes one or more of acrylonitrile, vinyl acetate, vinylidene chloride, styrene and methyl styrene.

16. The polymerizable monomer mixture of Claim 14 wherein the vinyl monomer mixture comprises, by weight:

from about 1% to about 15% (meth) acrylic acid,

from 0 to about 50% lower alkyl (meth) acrylate,

from about 25% to 99% upper alkyl (meth) acrylate; and the resin is a hydrogenated hydrocarbon resin having from about 20% to about 65% aromaticity with a molecular weight of from about 1000 to about 2500.

17. The polymerizable monomer mixture of Claim 14 wherein the resin is a hydrogenated natural resin or terpene.

18. A pressure sensitive adhesive film comprising a film carrying a coating of an internally resin tackified acrylic copolymer comprising:

a hydrogenated hydrocarbon resin, having a molecular weight of from about 500 to about 5000 and an aromatic content of at least 10% by weight; and

an acrylic copolymer formed from alkyl (meth) acrylate and (meth) acrylic acid monomers, liquid at ambient temperatures, by free radical initiated polymerization of the monomers, in the presence of the resin in solution with the monomers, in amounts of from about 10 to about 100 parts resin per 100 parts of the monomers polymerized to form the copolymer latex composition.

19. The pressure sensitive film of Claim 18 wherein the copolymer coating is from 0.5 to about 1.5 mils thick.

20. The pressure sensitive film of Claim 18 wherein the monomer comprises from 2 wt.% to about 6 wt.% of a (meth) acrylic acid, from about 10 wt.% to about 35 wt.% of a lower alkyl (meth) acrylate acid, from about 60 wt.% to about 88 wt.% of an upper alkyl (meth) acrylate.

21. A laminating adhesive composition comprising a hydrogenated hydrocarbon resin, having a molecular weight of from about 500 to about 5000 and an aromatic content of at least 10% by weight; and

an acrylic copolymer formed by free radical initiated polymerization of a monomer mixture comprising alkyl (meth) acrylate and (meth) acrylic acid monomers, having dissolved therein, from about 10 to about 100 parts of the resin per 100 parts of the polymerizable monomers.

22. The laminating adhesive of Claim 21 wherein the hydrogenated hydrocarbon resin is a natural resin or terpene.

23. The tackified acrylic copolymer latex of Claim 21 wherein the monomer polymerized comprises from 1 to about 15 wt.% of a (meth) acrylic acid, 0 to about 50 wt.% of a lower alkyl (meth) acrylate ester and from about 25 wt.% to 99 wt.% of an upper alkyl (meth) acrylate ester.

24. The tackified acrylic copolymer latex of Claim 23 wherein the monomer comprises from 2% to about 6% of a (meth) acrylic acid, from about 10 wt.% to about 35 wt.% of a lower alkyl (meth) acrylate acid, from about 60 wt.% to about 88 wt.% of an upper alkyl (meth) acrylate.

25. A laminant comprising at least two layers of material bonded by an adhesive composition comprised of:

a hydrogenated hydrocarbon resin, having a molecular weight of from about 500 to about 5000 and an aromatic content of at least 10% by weight; and

an acrylic copolymer formed by free radical initiated polymerization of a monomer mixture comprising alkyl (meth) acrylate and (meth) acrylic acid monomers, having dissolved therein, from about 10 to about 100 parts of the resin per 100 parts of the polymerizable monomers.

26. The laminant of Claim 25 wherein the hydrogenated hydrocarbon resin is a natural resin or terpene.

27. The tackified acrylic copolymer latex of Claim 25 wherein the monomer polymerized comprises from 1 to about 15 wt.% of a (meth) acrylic acid, 0 to about 50 wt.% of a lower alkyl (meth) acrylate ester and from about 25 wt.% to 99 wt.% of an upper alkyl (meth) acrylate ester.

28. The tackified acrylic copolymer latex of Claim 27 wherein the monomer comprises from 2% to about 6% of a (meth) acrylic acid, from about 10 wt.% to about 35 wt.% of a lower alkyl (meth) acrylate acid, from about 60 wt.% to about 88 wt.% of an upper alkyl (meth) acrylate.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/03131

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: C 09 J 151/00, C 08 F 289/00, C 09 J 4/06, C 09 J 7/02, // (C 09 J 151/00, 145:00)

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^5	C 08 F, C 09 J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	EP, A, 0240253 (EXXON CHEMICAL PATENTS INC.) 7 October 1987 see page 12, lines 18-28 --	1,6
A	Patent Abstracts of Japan, volume 9, no. 82 (C-275)(1805), 11 April 1985, & JP,A, 59213783 (NIPPON SHOKUBAI KAGAKU KOGYO K.K.) 3 December 1984 see abstract cited in the application ----------	1,6

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
24th September 1990	16 OCT 1990
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Mme N. KUIPER [signature]

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9003131

SA 37710

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 10/10/90
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0240253	07-10-87	JP-A- 63301212	08-12-88

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82