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(54) **Title**: MONOBENZOATE USEFUL AS A PLASTICIZER/COALESCENT IN POLYMERIC DISPERSIONS

(57) **Abstract**: A unique monobenzoate useful as a plasticizer or coalescent for polymeric dispersions, including without limitation architectural and other coatings, paints, OEM coatings, special purpose coatings, overprint varnishes, inks, nail polish, floor polishes and the like. The monobenzoate comprises 3-pheny propyl benzoate, a benzoate ester previously known as a flavoring and fragrance agent, but not previously utilized as a plasticizer or coalescent in polymeric applications. The inventive monobenzoate provides a suitable non-phthalate, lower VOC content alternative plasticizer or coalescent that is compatible with a wide variety of polymers. Depending on the application, the advantages rendered by the use of the inventive monobenzoate include, among other things, excellent solvating properties, viscosity stability, improved rheology, good film formation and comparable or better gloss, hardness, adhesion, water and alkali resistance, scrub and rub resistance, block resistance, color density, dry to touch time, open time, and MFFT, compared with that achieved by traditional plasticizers or coalescents.

MONOBENZOATE USEFUL AS A PLASTICIZER/COALESCENT IN POLYMERIC DISPERSIONS

FIELD OF THE INVENTION

[0001] This invention is directed to a non-phthalate monobenzoate useful as a plasticizer or coalescent in a variety of polymer applications, including but not limited to architectural coatings, industrial coatings, OEM coatings, paints, enamels, lacquers, inks, overprint varnishes ("OPV's"), other coatings, polishes and the like. In particular, this invention is directed to the use of a monobenzoate ester, 3-phenyl propyl benzoate, in coatings applications, to provide compatibility, lower VOC content, and excellent film forming properties. Depending on the coatings application, the invention provides compositions that have comparable or better rheology, viscosity stability, compatibility, processability, gloss, hardness, scrub and rub resistance, water and alkali resistance, adhesion, color density, and film formation, among other advantages, over traditional plasticizers or coalescents.

[0002] The invention is also directed to polymeric compositions comprising the inventive monobenzoate, such as architectural and industrial coatings, paints, OEM coatings, special purpose coatings, OPV's, inks, nail polish, floor polish and other polymeric coatings.

BACKGROUND OF THE INVENTION

[0003] In polymer-based coating compositions, the film-forming aid, i.e., coalescent, is a very important component. Coalescents allow film formation to occur at lower temperatures than the polymer without the coalescent would. Typically, about 4°C is the temperature to which a coalescent must reduce the minimum film formation temperature (MFFT) of a polymer. In the case of a polymer having an already low MFFT, the coalescent provides formation of a film with improved properties as compared to a film without the coalescent. In the case of polymers having high glass transition temperatures (Tg), coalescents allow film formation to occur at desired ambient conditions, whereas a continuous film would not form with such polymers without the coalescent.

[0004] Coalescents partition to the polymer in the emulsion and soften dispersed particles allowing them to fuse or form a continuous film. The coalescent will then partially or completely volatilize out of the film, depending on the coalescent, allowing the film to regain its original physical properties. Plasticizers used as coalescents are less volatile and slower to come out of the film.

[0005] Besides facilitating continuous film formation at lower temperatures, coalescents are selected that improve the properties of the paint/coating film, such as gloss, scrub resistance, and block resistance. Coalescents are also selected based upon a variety of properties, including without limitation, volatility, miscibility, stability, compatibility, ease of use, and cost.

[0006] Plasticizers have been known and used for years in latex paints and other coatings, primarily for their excellent coalescent properties. In some instances, they are also desired for their plasticizer function at higher levels of use. A typical plasticizer softens a polymer and makes it more workable. It is also well-known that plasticizers can improve paint performance characteristics, such as mud cracking, wet edge and open time.

[0007] Of particular concern in selecting a plasticizer/coalescent for a coatings composition is the VOC content of the plasticizer/coalescent in the resulting film. By its nature, "escaping" or "volatilizing" coalescent contributes significantly to the VOC's of the film, beginning with the coalescing phase and lasting for a sustained period afterwards. This, in turn, can affect the air quality around the film and be manifested as an unpleasant odor. Traditional coalescents are highly volatile and can contribute significantly to the VOC content of a paint or coating and have significant environment and health disadvantages. VOC's readily vaporize or evaporate into the air, where they may react with other elements or compounds to produce ozone. Ozone, in turn, causes air pollution and a host of health concerns including breathing problems, headache, burning, watery eyes and nausea, just to name a few.

[0008] VOC's are of particular concern in the paint and coatings industry in the manufacture and application of products containing VOC's. Use of VOC's in the manufacture of paint and coatings result in poor plant air quality and worker exposure to harmful chemicals. Persons who are exposed to VOC's may suffer from a number of health problems, including but not limited to several types of cancers, impaired brain function, renal dysfunction and other health problems.

[0009] Similarly, painters and other users of VOC-containing paints and coatings who are regularly exposed to harmful VOC vapors may suffer from health problems. VOC-containing products release harmful VOC's into the air as they dry, and become especially concentrated in indoor applications. Indoor VOC levels are routinely 10 times higher than outdoor levels and may be up to 1,000 times higher immediately after painting. Further, although VOC levels are highest during and soon after painting, they continue seeping out for several years. In fact, only 50 percent of the VOC's may be released in the first year. Accordingly, paints and coatings having high VOC content are considered health and environmental hazards, and regulations have been implemented to protect manufacturing workers and end-users.

[0010] Waterborne overprint varnishes (OPV's) and inks are specific types of coatings that have significant roles in the graphic arts industry. OPV's provide the finishing touch to printed media, protecting ink and printed matter for a wide variety of applications, including but not limited to books, magazines, packaging materials, and other printed matter. These clear coatings also provide visual effects in addition to protecting the underlying ink from damage.

[0011] Various OPV's and inks exist having a wide range of compositions. OPV's and inks are selected for use based upon the printing process to be utilized and volume of use. OPV's most commonly comprise three forms: waterborne, UV-curable polymeric dispersions, or other solution (solvent) polymers. Waterborne OPV's are all based on polymeric dispersions having a variety of compositions and glass transition temperatures (Tg). A classic type of polymer used in polymeric dispersions, such as OPV's, is a hard styrene acrylic, which has excellent gloss and durability characteristics.

[0012] OPV's are often exposed to harsh conditions during processing and in use, yet must look perfect when finally placed on display. Hence, OPV's may contain various other additives to impart rub resistance and scratch and abrasion resistance. Still other additives may be selected to facilitate the formation of an effective barrier to moisture, oils or other soils and to improve heat resistance. The choice of additive may depend on the final use intended for the graphic art media prepared using an OPV and the volume of that anticipated use.

[0013] Many types of inks are utilized in the graphic arts industry to fit the various printing processes. Like OPV's, waterborne inks often comprise polymeric dispersions. Inks are often "coated" or protected with OPV.

[0014] As with architectural coatings (paints) and industrial coatings, formation of a continuous film that achieves proper performance is important in graphic arts applications. Waterborne OPV's and inks are coatings that may require a plasticizer/coalescent for proper film property development. Older generation polymeric systems used in OPV's have very high glass transition temperatures. These older generation systems, while not necessarily film formers at room temperature, provided excellent performance for different applications. To assist in the development of performance properties in these harder systems, the graphic arts industry utilizes coalescents to assist in film formation in waterborne OPV's and inks. These coalescents have also typically been the more volatile types. While they function well, VOC content is an issue with these types of coatings as well.

[0015] New generation polymer emulsions used in OPV's and inks seem to be following the same trends that are found in other coatings. These systems are softer and may not necessarily require any coalescent or plasticizer to form a film under their conditions of use. Heat and/or air flow may be employed to assist in coalescence in graphic arts. However, these approaches to coalescence may result in poor performance properties and their use is thus limited.

[0016] Traditional coalescents for paint include the traditional industry standard film-forming aid, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TXMB). Other coalescents of choice in different coating industry segments include glycol ethers. All of these are invariably 100% volatile by the EPA 24 D2369 volatility test, a method of VOC determination used for paint and other coating systems. The monobenzoate, 2-ethyl hexyl benzoate, has been used as a coalescent in OPV's and waterborne inks and is functional, but it still has a fairly high VOC content.

[0017] Consumers are demanding safer alternatives, and coatings formulators continue to be faced with the challenge of reducing VOC's, while, at the same time, providing a coating with required performance characteristics. Most often, formulators reduce the amount of the most volatile components used in the coatings or replace them with lower VOC content components, both of which reduce VOC concerns to some extent, but may result in compromised performance. Other approaches are to use soft polymers with no coalescent (with the sacrifice of performance in some instances), reduction or elimination of glycols used for antifreeze and tooling, or the use of a low VOC plasticizer or coalescent.

[0018] Plasticizers are useful coalescents for waterborne systems as they have low VOC contribution; however, they impart greater permanence, i.e., they are slower to leave film, and thus less volatile. In some instances, the permanence of plasticizers can be a detriment. In using plasticizers as coalescents, a balance must be struck between greater permanence — and thus lower VOC's — and good final film properties. Desirably, a low VOC content paint or coating should have, at a minimum, equivalent performance to paints or coatings having higher VOC content. Toward that end, raw material suppliers continue to develop new, lower VOC products for use in paints and coatings, which do not compromise performance.

[0019] Plasticizers traditionally used in the coatings industry (including graphic arts applications), include di-n-butyl phthalate (DBP), diisobutyl phthalate (DIBP) or butyl benzyl phthalate (BBP). These plasticizers were used when a true plasticizer was required, as is the case when polymers with high Tg's are employed in one application or another. DBP and DIBP have a lower VOC content than traditional coalescents, but are still somewhat volatile, while BBP has a very low VOC content. Apart from VOC content, however, phthalate ester use has some disadvantages, as DBP and BBP uses, in particular, are restricted due to regulatory concerns.

[0020] Dibenzoate plasticizers have well known utility in coatings. Dibenzoates by their nature are non-phthalates and do not have the restrictions or health concerns associated with phthalates. Benzoates are historical alternatives for the graphic arts industry. Classic dibenzoates used as coalescents include DPGDB as well as blends of DEGDB and DPGDB. Commercial examples of benzoates include K-Flex® DP (DPGDB), K-Flex® 500 (DEGDB/DPGDB blend), K-Flex® 850S (a newer grade of

DEGDB/DPGDB blend), and K-Flex® 975 P (a new triblend comprising DEGDB/DPGDB/1,2-PGDB), among many others.

[0021] Monobenzoate esters known to be useful as plasticizers include: isodecyl benzoate (IDB), isononyl benzoate (INB), and 2-ethylhexyl benzoate (EHB). For example, isodecyl benzoate has been described as a useful coalescent agent for paint compositions in U.S. Patent No. 5,236,987 to Arendt. The use of 2-ethylhexyl benzoate in a blend with DEGDB and diethylene glycol monobenzoate is described in U.S. Patent No. 6,989,830 to Arendt et al. The use of isononyl esters of benzoic acid as film-forming agents in compositions such as emulsion paints, mortars, plasters, adhesives, and varnishes is described in U.S. Patent No. 7,638,568 to Grass et al.

[0022] "Half ester" monobenzoates include dipropylene glycol monobenzoate and diethylene glycol monobenzoate, which are byproducts of the production of dibenzoates, but which, most of the time, are not objects of production. Half esters are not known for being high solvators and are less compatible than the corresponding dibenzoate in PVC. However, the half esters are compatible with emulsion polymers, such as acrylic and/or vinyl ester polymers, which are commonly used in paint and coatings applications.

[0023] There remains a need for non-phthalate, low VOC plasticizers and coalescents for use in coatings applications. Such alternatives should be compatible with a wide variety of polymers and have lower VOC content and comparable or better performance properties when used in coating applications traditionally requiring plasticizers and/or coalescents. Non-phthalate, low VOC alternatives are particularly desirable in view of the environmental, health and safety issues associated with many traditional plasticizers and coalescents.

[0024] It has been discovered that an entirely different monobenzoate, 3-phenyl propyl benzoate (3-PPB), is a surprisingly effective lower VOC plasticizer alternative, as compared to TXMB, IDB or INB, for use in polymeric applications, including but not limited to paints and other coatings, OPV's and inks. Advantages of this monobenzoate, besides lower VOC's, are its excellent health, safety and environmental profile and handling properties, which are better than most dibenzoates and monobenzoates previously used. This new monobenzoate is not classified as hazardous under any "hazard" class, and no labeling elements are required.

[0025] The monobenzoate, 3-PPB, has not been utilized in polymeric applications of the type discussed herein in the past. It has been used and continues to be used in flavoring and fragrance applications. It has also been used as a solubilizer for certain active or functional organic compounds in personal care products as described in U.S. Patent Publication 2005/0152858.

[0026] While this invention is focused on the use of the inventive plasticizer in paints and other coatings, other applications for the inventive monobenzoate include plastisols, adhesives, sealants and caulks, which are the subject of co-pending applications.

[0027] It is an object of the invention to provide a non-phthalate plasticizer/coalescent having excellent compatibility with a wide variety of polymers and a lower VOC content than traditional plasticizers or coalescents, for use alone or in combination with other plasticizers/coalescents in paints, architectural coatings, industrial coatings, OEM coatings, special purpose coatings, lacquers, enamels, OPV's, inks, polishes and other polymeric coatings where plasticizers and coalescents are traditionally required.

[0028] It is a further object of the invention to provide a monobenzoate useful as a coalescent in polymeric dispersions, such as OPV's and inks, which has a lower VOC content and achieves comparable or better performance than traditional coalescents, including but not limited to compatibility, gloss, hardness, water and alkali resistance, adhesion, dry to touch time, color density and film formation.

[0029] Yet another object of the invention is to provide a monobenzoate useful as a coalescent in polymeric dispersions, which has a lower VOC content and achieves comparable or better performance than traditional coalescents, including but not limited to efficiency and compatibility when used in traditional latex emulsions or other polymeric coatings.

[0030] It is a further object of the invention to provide a polymeric emulsion coating having a low VOC content and improved performance properties, including without limitation viscosity, hardness, gloss, block resistance, scrub and rub resistance, chemical resistance, dry time, open-time/wet edge, mudcrack resistance, and heat age stability over that achieved with current low VOC emulsion coatings.

[0031] It is yet another object of the invention to provide a low VOC content polymer emulsion coating that is environmentally friendly, safe to handle and not subject to regulatory control.

[0032] Still a further object of the invention is to provide a monobenzoate plasticizer, useful as a plasticizer alone or in a blend of plasticizers, for use in paint or other polymeric coatings, which has a lower VOC content and comparable or better performance than traditional coalescents.

[0033] Other objects of the invention will be apparent from the description herein.

SUMMARY OF THE INVENTION

[0034] This invention is directed to a non-phthalate benzoate plasticizer useful as coalescent for polymeric dispersions, such as architectural coatings (paint), industrial coatings, OPV's, inks, and polishes, among others. In particular, the invention is directed to the use of a new monobenzoate, 3-phenyl propyl benzoate (3-PPB), a component not previously known or used as a plasticizer or coalescent for coating applications.

[0035] Use of the inventive monobenzoate in the same or similar amounts as traditional plasticizers/coalescents results in a lower VOC content and comparable or better performance and handling properties than that achieved with traditional plasticizers or coalescents. The inventive monobenzoate has low toxicity and does not have the environmental, health and safety issues associated with traditional phthalate plasticizers or coalescents.

[0036] In one embodiment, the invention is a non-phthalate coalescent, 3-PPB, useful in coatings applications to aid film formation and improve properties such as viscosity, gloss, block resistance, scrub and rub resistance, chemical resistance, dry time, open-time/wet edge, mudcrack resistance, and heat age stability. In another embodiment, the invention is an architectural coating, paint, industrial coating, OEM coating, special purpose coating, lacquer, enamel, OPV, ink, nail polish, or floor polish, comprising 3-PPB.

[0037] In a further embodiment, the invention is a variety of aqueous or non-aqueous polymer compositions comprising 3-PPB.

[0038] In still another embodiment, the invention is a blend of 3-PPB with other plasticizers and coalescents, including solid plasticizers, for use in paint, OPV's, waterborne inks, colorants, and other coatings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0039] FIG. 1 shows the volatility characteristics determined for the neat plasticizers evaluated, using ASTM D2369, 110° C for one hour.

[0040] FIG. 2 shows the volatility characteristics determined for the neat plasticizers evaluated, using a TGA isothermal scan at 110° C for one hour.

[0041] FIG. 3 illustrates the viscosity response of the binary blends comprising various plasticizers/coalescents.

[0042] FIG. 4 shows the amount of water required to reduce the viscosity to 150 mPa•s, a nominal viscosity for comparison.

[0043] FIG. 5 shows the MFFT of the binary blends at plasticizer/coalescent levels of 4% wet.

[0044] FIG. 6 shows the MFFT of the binary blends at plasticizer/coalescent levels of 4, 6 and 8% wet.

[0045] FIG. 7 shows the OPV viscosity response obtained with 4% plasticizer/coalescent at 1 day aging.

[0046] FIG. 8 shows the time to dry to touch for OPV's comprising various plasticizers/coalescents.

[0047] FIG. 9 shows the gloss data obtained for the OPV's comprising various plasticizers/coalescents (20° gloss on a 3B Leneta substrate).

[0048] FIG. 10 shows Konig hardness data obtained for the OPV's comprising various plasticizers/coalescents.

[0049] FIG. 11 shows block resistance results for the semigloss acrylic at 1-day (RT and 120°F) for the plasticizers/coalescents evaluated.

[0050] FIG. 12 shows block resistance results for the semigloss acrylic at 7-day (RT and 120° F).

[0051] FIG. 13 shows the scrub resistance results for the semigloss acrylic for the plasticizers/coalescents evaluated.

[0052] FIG. 14 shows open-time, wet edge results of the semigloss acrylic for the plasticizers/coalescents evaluated.

[0053] FIGS. 15 (a) and (b) show heat age stability of the semigloss acrylic, both Delta Viscosity and Delta E Color Shift, respectively, for the plasticizers/coalescents evaluated.

[0054] FIG. 16 shows the mudcrack resistance of the semigloss acrylic for the plasticizers/coalescents evaluated.

[0055] FIG. 17 shows the low temperature, touch-up results of the semigloss acrylic for the plasticizers/coalescents evaluated.

[0056] FIG. 18 shows the block resistance, 7-day results (RT and 120° F) for the vinyl acrylic flat paint for the plasticizers/coalescents evaluated.

[0057] FIG. 19 shows the scrub resistance results of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated.

[0058] FIG. 20 shows the open-time/wet-edge results of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated.

[0059] FIGS. 21 (a) and (b) show the heat age stability of the vinyl acrylic flat paint, both Delta Viscosity and Delta E color shift results, respectively, for the plasticizers/coalescents evaluated.

[0060] FIG. 22 shows the mudcrack resistance results of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated.

[0061] FIG. 23 shows the low temperature touch-up results of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated.

DETAILED DESCRIPTION OF THE INVENTION

[0062] The present invention is directed to a monobenzoate plasticizer useful as a primary or secondary plasticizer/coalescent for aqueous and non-aqueous based polymer coatings, including but not limited to architectural coatings (paint), industrial coatings, OEM coatings, special purpose coatings, OPV's, inks and polishes. The benzoate plasticizer comprises a unique monobenzoate, 3-phenyl propyl benzoate (3-

PPB), a known flavor and fragrance component, not previously known or used as a plasticizer or coalescent in polymeric coatings.

[0063] The inventive monobenzoate plasticizer can generally be utilized as a primary plasticizer, a secondary plasticizer in blends with other plasticizers, or a coalescent with numerous polymeric dispersions, often as a substitute or alternative for conventional plasticizers/coalescents having a higher VOC content. Any of the known polymers that can be formulated into an architectural coating (paint), industrial coating, OEM coating, special purpose coating, nail polish, OPV, ink, floor polish or other similar polymeric coating can be used in combination with the inventive monobenzoate to prepare a low VOC content composition in accordance with the present invention.

[0064] Polymers useful to prepare the polymeric dispersions discussed herein are known in the art. The inventive composition is expected to be useful with a wide variety of polymers, including both waterborne and non-aqueous-based polymer compositions. Suitable polymers include, but are not limited to: various vinyl polymers, such as polyvinyl chloride and copolymers thereof, vinyl acetate, vinyl acrylates, vinyl chloride co- and ter-polymers, vinylidene chloride, diethyl fumarate, or diethyl maleate; various polyurethanes and copolymers thereof; cellulose nitrate; polyvinyl acetate and copolymers thereof; various polyacrylates and copolymers thereof, and various esters of versatic acid.

[0065] Acrylic polymer compositions for various applications may also be used with the inventive monobenzoate and include various polyalkyl methacrylates, such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, cyclohexyl methacrylate, or allyl methacrylate; or various aromatic methacrylates, such as benzyl methacrylate or styrene acrylate; or various alkyl acrylates, such as methyl acrylate, ethyl acrylate, butyl acrylate, or 2-ethylhexyl acrylate; or various acrylic acids, such as methacrylic acid and other styrenated acrylics.

[0066] Other polymers for which the inventive monobenzoate may be useful as a plasticizer include epoxies, polyamides, and nitrocellulose. Still other polymers will be evident to one skilled in the art.

[0067] Use of the inventive monobenzoate is not limited to any particular polymer. Although the invention is described primarily with respect to paint, OPV and ink applications, the inventions is not limited as such. Other polymer-based coating compositions requiring plasticizers and/or coalescents and/or where plasticizers and/or coalescents are traditionally utilized, are known to one skilled in the art. The novel monobenzoate of the present invention may be used as a low VOC substitute or alternative for various traditional polymeric dispersions.

[0068] The total amount of the inventive monobenzoate used in any particular polymeric dispersion would range broadly depending on the particular polymer, the characteristics of the polymer and other components, the process, the application or use and the results desired. Exemplary amounts for plasticizers/coalescents are included in the examples and further described generally herein.

[0069] Generally, the amount of coalescent required for a polymeric dispersion is based on the MFFT of the base polymer and may be used in an amount sufficient to form a film at room temperature. The harder the polymer (higher MFFT and Tg), the more plasticizer/coalescent required.

[0070] In paints or coatings, plasticizer/coalescents can be used in amounts up to about 20% of the polymer solids in the system, depending on the particular polymer.

[0071] In OPV's and inks, coalescents may be utilized in amounts up to about 20 wt. %, based upon the total weight of the overprint varnish or ink. Exemplary amounts may range from about 2% to about 8 % wet.

[0072] Useful amounts of 3-PPB are set forth in the examples. It is expected that one skilled in the art would be able to arrive at additional acceptable amounts for other applications, based on the intended use and desired performance in the particular polymeric application.

[0073] Other applications for the inventive monobenzoate include nail polish, floor polish, OEM coatings, and special purpose coatings. For nail polish products, in particular, phthalates have been used for at least a decade, and certain dibenzoates have also been utilized for several years, wherein the advantages attributable to coalescents discussed herein are desired.

[0074] The inventive monobenzoate may be, but is not required to be, blended with various other conventional plasticizers to enhance or augment properties of polymer compositions. Conventional plasticizers have been described herein and include, but are not limited to phthalate esters up to C5, phosphate esters, polyesters, citrates, isobutyrates, sulfonamides, sulfonic acid esters, terephthalate esters up to C4, epoxy plasticizers, benzoate esters, including both di- and mono-benzoates, or mixtures thereof.

[0075] The inventive monobenzoate may also be blended with solid plasticizers, such as sucrose benzoate, dicyclohexyl phthalate, triphenyl phosphate, glycerol tribenzoate, 1,4-cyclohexane dimethanol (CHDM) dibenzoate, pentaerythritol tetrabenzoate, alkyl glycol esters, or mixtures thereof.

[0076] The inventive monobenzoate may be combined with or include various amounts of conventional additives such as oils, diluents, antioxidants, defoamers, surfactants, heat stabilizers, flame retardants, surfactants, waxes, solvents and the like, depending on the particular coatings application. Additives amounts can generally vary widely and often range from about 0.1 to about 75 parts by weight for every 100 parts by weight of the coating composition.

[0077] By way of example, traditional OPV's, in addition to the coalescent, comprise a dispersion of a high Tg (>10° C) polymer, wax dispersions, various high Tg resins, surfactants, defoamers, and water. Traditional inks, in addition to the coalescent, comprise similar components as an OPV, but with added pigments for color.

[0078] Other useful components for the various polymer applications are known to one skilled in the art. Exemplary simple basic OPV's and inks and paint formulations are set forth in the examples.

[0079] The inventive monobenzoate provides a lower VOC content alternative over many traditional coalescents and, depending on the application, provides comparable or better compatibility, viscosity stability, rheology, film formation, gloss, water and alkali resistance, dry to touch time, open time, scrub and rub resistance, color density, adhesion, peel strength and hardness, among other advantages. In many instances, the inventive monobenzoate outperforms industry standard coalescents, regardless of VOC content, including traditional and newer dibenzoate blends. The monobenzoate is particularly useful as a coalescent when considering the use of harder polymers as alternatives to softer polymers in a variety of low VOC formulations.

[0080] The invention is further described by the examples set forth herein.

[0081] Examples

[0082] The evaluation of the plasticizers/coalescents consisted of a variety of experiments. First, VOC's of the neat plasticizers/coalescents selected were determined. Then, effectiveness and efficiency of the coalescents with a traditional polymer were determined using simple binary blends.

[0083] In another segment, a starting basic OPV formulation was prepared to assess the effect of the new plasticizer in an actual OPV. In yet another segment, the coalescent performance in a simple waterborne model ink formulation was evaluated. Inks were then coated with the experimental OPV's and evaluated.

[0084] Other evaluations involved the use of the inventive monobenzoate in adhesives and plastisols and are set forth herein below.

[0085] Examples 1-4 – *OPV and Inks*

[0086] The polymer selected for use in the OPV/ink examples was a traditional high Tg, hard styrene acrylic emulsion, a standard in the graphic arts industry, although it is expected that the present inventive coalescent would be useful in a large number of polymeric dispersions used in this industry. Such polymers would be known to one skilled in the art. The polymer was utilized in all of the simple starting formulations set forth herein.

[0087] The following plasticizers/coalescents were selected for evaluation in the examples (in whole or part):

- 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (TMPDMB). This coalescent is historically the traditional coalescent of choice in paint and other coatings but not necessarily in OPV's or inks.
- 2-Ethylhexyl benzoate (2-EHB). This coalescent was introduced a few years ago as a new lower VOC type coalescent.
- Butyl Carbitol™ diethylene glycol monobutyl ether (BC)
- Carbitol™ diethylene glycol monomethyl ether (C)
- Butyl Cellosolve™ ethylene glycol monobutyl ether (BCL)
- Dipropylene glycol monomethyl ether (DPM)
- Diethylene glycol dibenzoate (DEGDB)
- Di-n-butyl phthalate (DBP)

- Butyl benzyl phthalate (BBP)
- Traditional diblend of diethylene glycol dibenzoate and dipropylene glycol dibenzoate (CB1)
- K-Flex® 975P (X 20), a dibenzoate triblend comprising DEGDB, DPGDB and PGDB in specified proportions (80 wt.% of a 4:1 DEGDB:DPGDB and 20 wt.% PGDB)
- K-Flex® 850S (X-250), a newer dibenzoate diblend of DEGDB and DPGDB
- X-613 the inventive monobenzoate, 3-phenyl propyl benzoate (3-PPB)

[0088] The plasticizers/coalescents and TMPDMB are not soluble in water but the DPM, BCL and C are completely or partially soluble in water. It is expected that the water insoluble plasticizers/coalescents will partition to the polymer in the dispersion.

[0089] The following raw materials were used in the formulations prepared for Examples 1-4:

[0090] Raw Materials

Description	**Tradename**	**Manufacturer**
Styrene Acrylic emulsion, high Tg	Joncryl™ 89	BASF
Resin solution, 34%, high Tg	Joncryl 60	BASF
Wetting Surfactant	Efka™ 3580	BASF
Defoamer	Efka 2580	BASF
Blue Pigment dispersant, 48% solids	Generic	Several
PE wax dispersion, 26% solids	Joncryl Wax 26	BASF
X-20, X-250, X-613, commercial binary dibenzoate blend, DEGDB	Experimental or K-Flex®	Emerald Kalama Chemical, LLC
2,2,4-trimethyl-1,3-pentanediol monoisobutyrate	Various	Various
Dipropylene glycol monomethyl ether	Dowanol™	DOW
Diethylene glycol monobutyl ether	Butyl Carbitol™	DOW
Diethylene glycol monomethyl ether	Carbitol™	DOW
Ethylene glycol monobutyl ether	Butyl Cellosolve™	DOW
Diethylene glycol dibenzoate	K-Flex® DE	Emerald Kalama Chemical, LLC

[0091] Tests Utilized – The following tests were employed:

- On neat plasticizers - EPA 24, ASTM D2369 volatility, 110°C for one hour; and a TGA isothermal scan at 110°C.
- On binary polymer emulsion/coalescent blend – MFFT, viscosity response of base emulsion with the coalescent, and viscosity reduction.
- On OPV's – Viscosity, MFFT's, gloss, water resistance, alkali resistance, hardness, and dry to touch.
- In ink - Rub resistance, adhesion, gloss, optical density, and ink viscosity.

[0092] Test Methodology – Specific details of the test methods are described below:

[0093] Volatility: ASTM D2369 used. A TGA isothermal for one hour under air at 110°C was also employed.

[0094] Viscosity Response: Both the initial and 24 hour viscosities were measured. Viscosity measurements were made using a Brookfield RVT at 20 RPM's for 10 revolutions at 23 ± 2°C.

[0095] MFFT (Minimum Film Formation Temperature): The MFFT's were measured with a Rheopoint MFFT 90 under air. ASTM D2354-10 employed.

[0096] Gloss: The gloss of the substrate or the print was measured at 20° and 60° with a Micro-TRI-Gloss II Meter. ASTM D523 employed.

[0097] Water Resistance: Two drops of distilled water was applied to the print, covered with a watch glass, and timed for 2, 5 or 10 minutes. After the allotted time, the water was removed gently with a folded Kimwipe. The print and Kimwipe™ tissue were examined and rated. The rating was: 5 – no effect; 4 – slight blush; 3 – blush; 2 – partial break; 1 – total break in film.

[0098] Alkaline Resistance : Two drops of alkaline solution (Clorox® Formula 409) was applied to the print, covered with a watch glass, and timed for 2, 5 or 10 minutes. After the allotted time, the solution was removed gently with a folded Kimwipe™. The print and Kimwipe™ were examined and rated. The rating was: 5 – no effect; 4 – slight blush; 3 – blush; 2 – partial break; 1 – total break in film.

[0099] Rub Resistance: Rub resistance was evaluated using 5 layers of cheesecloth under a 1 kg weight. The cheesecloth and the weight were rubbed against the ink or the OPV covered ink 100 times. The cheesecloth was then evaluated and rated. The rating was - 5 – no effect; 4 – slight blush; 3 – blush; 2 – partial break; 1 – total break in film.

[0100] Hardness: The OPV was coated on an aluminum panel using a 3 mil drawdown. Samples were then dried for 4 hours and tested using a Konig Pendulum Tester. Samples were tested 4 hours, 24 hours, 3 days and 7 days after preparation. ASTM D4366 employed.

[0101] Adhesion to Prints: Scotch tape was pressed firmly to the print surface and then pulled off at a 90° angle as fast as possible while holding the print down. ASTM D3359-9

[0102] Optical Density and Color of Ink: The optical density (color strength) of the prints was measured with an X-Rite Color i7 spectrophotometer. ASTM D2066 employed.

[0103] Viscosity of Ink: The viscosity of the ink prepared was determined with a TA AR2000ex rheometer. Two centimeter plates with a gap of 100 microns were used at 25°C. The shear rate was 100 sec $^{-1}$.

[0104] Basic Preparation/Applications – Processes and techniques utilized in the evaluations are described in more detail below:

[0105] Formulation Preparation:

[0106] Diblend Formulations: Made by adding the coalescent slowly to the emulsion at 500 RPMs using a high speed mixer equipped with a Jiffy blade. Once the coalescent was added, the speed was increased to 750 RPM for a total mix time of 30 minutes.

[0107] Basic OPV Formulations: Prepared by adding the individual components in order to the mixing vessel while mixing at 500 RPM's using a high speed mixer equipped with a jiffy blade. The coalescent was the last to be added. This mixture was stirred for a total of 5 minutes at 500 RPM's after the add of the last component, then the speed of the mixer was increased to 750 RPM's for an additional 5 minutes.

[0108] Waterborne Phthalol Blue Flexographic Dispersion Ink: Individual components were added together slowly in the order listed with the wax dispersion added last. The ink was stirred with a high speed mixer at 500 RPM's with a jiffy blade for 5 minutes.

[0109] Test Panel Sample Preparation Conditions:

[0110] The gloss, water resistance, alkaline resistance, rub resistance and adhesion to the prints were evaluated both when the prints were first made, and after aging for 3 days. The OPV was applied with a #6 Mayer wound rod, depositing approximately 15μm wet film on a 3B Leneta card, a clay coated board or over a blue flexographic ink on a 3B Leneta card, oxidized polypropylene film or clay coated board.

[0111] Hand Proof Preparations:

[0112] The inks were drawn down with a Flexo Hand-proofer with a 180 pyramid cell anilox roll on 3B Leneta cards, clay coated boards and the treated polypropylene film. The ink was air dried and then dried in an oven three times for 30 seconds at 70°C.

[0113] OPV Over Ink Preparations:

[0114] The OPV was applied as above over the hand proofs and was air dried, then dried in an oven three times for 30 seconds at 70°C. Each OPV was matched with the corresponding ink in every case.

[0115] Example 1 – *VOC/Volatility of Neat Plasticizers/Coalescents*

[0116] Figures 1 and 2 illustrate the volatility characteristics determined for the neat plasticizers/coalescents evaluated. Traditional ether coalescents were definitely volatile. The plasticizers of the evaluation were all low in volatility and, thus, would not contribute significantly to the overall VOC of a formulation at typical levels of use. Conversely, the coalescents that were 100% volatile will contribute significantly to the total VOC release.

[0117] Of the benzoate coalescents evaluated, other than 2-EHB, the TGA scan data shows that the monobenzoate of the invention, X-613 (3-PPB), was the most volatile. However, X-613 was significantly lower in VOC content than the older traditional high VOC coalescents. All of the plasticizers/coalescents of the evaluation were considerably lower than 20% volatile compared to the ethers, TMPDMB and 2-EHB.

[0118] Example 2 — *Binary Blends of Coalescent and Polymer*

[0119] For this example, the binary blends evaluated are shown below.

Binary Blends

Raw Material	**Level, Percent**
Polymer dispersion, emulsion, Tg = 94°C	100, 96, 94 or 92
Coalescent/Plasticizer	0, 4, 6, or 8

[0120] Coalescents were incorporated in a base emulsion at the level of use in a basic starting OPV formulation (4%) to observe the effect of just the coalescent on the base polymer. The important tests to evaluate how coalescents affect the polymer are: viscosity response (indicates interaction and swelling of the polymer), minimum film formation temperature (MFFT), and water reduction.

[0121] Viscosity Response

[0122] The viscosity response of the base emulsion is indicative of the compatibility of the water insoluble coalescents tested. Figure 3 illustrates the viscosity response of the binary blends comprising various plasticizers/coalescents. With the exception of TMPDMB, all of the water insoluble coalescents had excellent viscosity response. The result for TMPDMB indicated that it lacked complete compatibility with the base styrenated acrylic polymer used in the blend.

[0123] Water Reduction

[0124] As the viscosity of an OPV is normally reduced to a constant value to allow the application at the same viscosities, the amount of water required to get the desired viscosity was determined and is illustrated in Figure 4. Figure 4 shows the amount of water required to reduce the viscosity to 150 mPa•s, a nominal viscosity for comparison. The amount of water required in each was as would be expected based on the initial viscosity, and infers that water dilution that can be achieved for the plasticizer/coalescent used.

[0125] MFFT

[0126] Figure 5 shows the MFFT of the binary blends with 4% wet plasticizer/coalescent added. Note that this low level of plasticizer had a very positive effect on the reduction of MFFT of the base polymer but did not bring it anywhere near room temperature. This is because a simple binary blend was evaluated, which is not yet a complete formulation.

[0127] As the MFFT of the binary blends were significantly higher than room temperature, it was decided to prepare blends with 6 and 8% wet plasticizer levels and determine their MFFT's. The results of that testing are illustrated in Figure 6.

[0128] The data developed were quite interesting and somewhat unexpected. The mono and dibenzoates decreased the MFFT significantly as might be expected. Interestingly, the films formulated with TMPDMB had significantly higher MFFT's at all coalescent levels than the other films. It was also noted that the TMPDMB films were especially difficult to read on the MFFT bar due to the mottled film quality caused by the poor compatibility of TMPDMB with the styrenated acrylic polymer emulsion. Because of this obvious incompatibility, the use of TMPDMB was discontinued for the remaining segments of the evaluation. The Carbitol and Butyl Cellusolve neither increased nor decreased MFFT. This would suggest a degree of incompatibility with the base polymer. X-20 (dibenzoate triblend) seemed to be particularly effective in MFFT suppression as was X-613 (the inventive monobenzoate). This effect has been noted in other polymers.

[0129] The next step in this evaluation was to see if the experimental plasticizers/coalescents can perform as required in a basic starting formulation at the level of test in the binary blends.

[0130] Example 3 – *Overprint Varnish*

[0131] <u>Viscosity Response</u>

[0132] Plasticizers/coalescents (at a level of use of 4%) were incorporated in the basic starting formulation listed in Table 1. The viscosity response and dry film properties were determined.

Table 1. Basic Overprint Varnish Formulation

Ingredient	**No Coalescent (%)**	**Coalescent (%)**
Styrene acrylic emulsion, high Tg	64	60
PE wax dispersion, 26% solids	4	4
Resin solution, 34%, high Tg	20	20
Wetting surfactant	4	4
Defoamer	0.1	0.1
Water	7.9	7.9
Plasticizer	0	4

[0133] The viscosity response of the base emulsion is indicative of the compatibility of the plasticizer/coalescent tested. Figure 7 illustrates the OPV viscosity response obtained with 4% plasticizer/coalescent at 1 day aging. The viscosities of the dibenzoate OPV's were all in the range expected -- the triblend X 20, the inventive monobenzoate X 613 and the diblend X 250 were comparable to DEGDB, 2-EHB, and BC (diethylene glycol monobutyl ether) (in the 100-150 mPa range). Viscosity response for DPM was lower. This coalescent is water soluble and did not partition (at least not completely) to the polymer.

[0134] The viscosity response to select dibenzoates in the OPV formulation with 6% coalescent instead of 4% was also measured. Both the X-250 and X-20 OPV's had viscosity of 250 mPa•s, which demonstrated that a relatively low add level (increase of 2%) had a significant impact on OPV viscosity with these types of plasticizers/coalescents.

[0135] MFFT

[0136] Table 2 lists the MFFT's obtained for the OPV formulations. All of the formulations formed films well at room temperature conditions. The water soluble coalescent types were more effective in MFFT suppression. As the MFFT depression was somewhat less for the dibenzoates than the ethers, the MFFT's of OPV's with loading at 6% wet on the two dibenzoate blends discussed above (X250 and X20) were also determined. These results are also listed in Table 2 and indicate that less than an additional 2% would be necessary to achieve results similar to the ethers. Most likely, 2% additional plasticizer would not be necessary to achieve the desired development of full performance characteristics.

Table 2. Minimum Film Formation Temperatures

OPV Coalescent	**Temperature, °C**	
	4%	**6%**
No Coalescent	31	31
X-20	7.2	- 4
X-250	7.2	- 5
DEGDB	6.1	-----
X-613	8.6	-5
2-EHB	7.2	-----
BC	-1.0	-----
DPM	-1.0	-----

[0137] Dry Time

[0138] One question addressed with respect to the use of real plasticizers instead of a volatile coalescent was the effect on parameters such as dry time. The dry to touch time of the OPV's was determined and is shown in Figure 8. Note that no significant difference in time to dry was noted between the volatile and non-volatile plasticizers or coalescents.

[0139] Gloss

[0140] Figure 9 lists the gloss data obtained for the OPV's. There was little difference in the 20° gloss values between the formulations with or without coalescents. This was likely due to the use of the solution resin and its contribution to gloss in the total formulation as well as the coalescent/plasticizer level.

[0141] Water and Alkali Resistance

[0142] Tables 3, 4 and 5 list the water and alkali resistance of the evaluation OPV's. The water resistance initial 1 day OPV on Leneta 3B charts was not nearly as good as the films aged for 3 days. The initial water resistance of the benzoate plasticized films were not as good as could be expected, as plasticizers will normally improve the water resistance of a film. Other factors in the formulation seem to come to bear in the OPV. After three days the water resistance was improved. On the clay coated board the benzoate films have good initial water resistance.

[0143] In the case of alkali resistance the properly coalesced films seemed to function marginally better than the film without coalescent or plasticizer.

Table 3. Water Resistance – Leneta 3B Substrate

Leneta 3B Substrate	**1 Day Dry**			**3 Day dry**		
	2 Min	**5 Min**	**10 Min**	**2 Min**	**5 Min**	**10 Min**
No Coalescent	5	5	4	5	5	5
X-20	4	4	2	5	5	5
X-250	4	3	2	5	5	5
DEGDB	4	3	3	5	5	5
X-613	4	4	5	5	4	5
2-EHB	4	4	4	5	4	5
BC	5	4	3	5	5	5
DPM	5	4	4	5	5	5

Rating system – 5 best; 1 worst

Table 4. Water Resistance – Clay Coated Board Substrate

	1 Day Dry			**3 Day Dry**		
Coalescent in OPV	**2 min**	**5 min**	**10 min**	**2 min**	**5 min**	**10 min**
No Coalescent	4	3	3	3	3	2
X-20	5	5	4	5	4	3
X-613	5	4	4	4	4	3
DPM	4	3	3	3	3	3
BC	4	3	3	3	2	2
X-250	5	4	4	4	4	3

Table 5. Alkaline Resistance - Clay Coated Board Substrate

Coalescent in OPV	**1 Day Dry**			**3 Day Dry**		
	2 Min	**5 Min**	**10 Min**	**2 Min**	**5 Min**	**10 Min**
No Coalescent	2	2	2	2	1	1
X-20	3	2	3	2	2	1
X-250	3	2	2	2	2	2
DEGDB	3	2	2	2	2	2
X-613	3	2	2	2	2	1
2-EHB	4	2	3	2	2	1
BC	3	2	2	2	2	1
DPM	3	3	2	2	2	1

[0144] Hardness

[0145] Figure 10 displays the hardness data obtained for the OPV's. Plasticizers often get a bad rap in coatings, where the belief is that as they are more permanent than coalescents they will stay and soften the films too much, resulting in poor performance. The data presented in Figure 10 is contrary to the "too soft" statement, disproving this generally held misbelief. In a properly formulated coating that meets coalescent expectations, low VOC plasticizers/coalescents will not necessarily soften too much. The 6% plasticizer films are somewhat softer, but they are somewhat over coalesced. Less is better and acceptable. The 4% OPV's are all similar to the much more volatile coalesced OPV's.

[0146] Example 4 – *Waterborne Ink*

[0147] Basically a waterborne ink is an OPV with color added. Inks were prepared based on each coalescent/plasticizer using the basic formulation set forth in Table 6 below.

Table 6. Basic Blue Waterborne Ink Formulation

Ingredient	**Without Coalescent (%)**	**With Coalescent (%)**
Styrene Acrylic emulsion, high Tg	43.1	39.1
Resin solution, 34%, high Tg	14	14
Wetting surfactant	2	2
Defoamer	0.1	0.1
Water	2.5	2.5
Plasticizer	0	4
Blue Pigment dispersant, 48% solids	37.1	37.1
PE wax dispersion, 26% solids	1.2	1.2

[0148] The ink was used under an OPV having the same coalescent/plasticizer type. In each case, plasticizer/coalescent was present at 4% in the ink and the OPV. The focus of this example is on the inventive monobenzoate, X-613.

[0149] The viscosities obtained for the inks were 317 mPa·s for the "no coalescent" ink, 758 mPa·s for X-613 ink, 411 mPa·s for DPM ink and 251 mPa·s for the C ink. Again, lower viscosities were noted for the inks having water soluble coalescents.

[0150] Tests were conducted on prints made with a hand proofer. Gloss, rub resistance, adhesion and color density on the ink were performed after the OPV was placed over the ink and dried.

[0151] Gloss

[0152] Table 7 lists the gloss data obtained on the OPV over ink. Plasticizers/coalescents improve gloss. X-250 was the best of the plasticizers in this respect and similar to the ether coalescent.

Table 7. 20° Gloss of Ink and OPV – Leneta 3B Substrate

Coalescent in Ink and OPV	**1 Day Dry**	**3 Day Dry**
Blank Card	58.9	55.3
No Coalescent	84.4	77.9
X-613	87.3	80.3
DPM	90.5	89.2
C	85.0	86.3

[0153] Rub

[0154] Table 8 lists the rub data obtained for the inks and the inks coated with OPV on Leneta 3B and on a polypropylene film. The OPV significantly improved the rub resistance of the film. No significant differences in the performance between the evaluation ink and OPV's was noticed.

Table 8. Rub Test

Coalescent In Ink and OPV	**Leneta 3B Substrate**		**Oxidized Polypropylene**	
	Only Ink	**OPV covered Ink**	**Only Ink**	**OPV covered Ink**
No Coalescent	3	4	2	4
X-613	2	4	3	4
DPM	2	4	2	4
C	3	4	2	4

[0155] Adhesions

[0156] Tables 9, 10 and 11 list the tape adhesion data obtained for the OPV/ink. On the sealed substrate, the coalesced films seem to function better, both initially and after 3 days of dry. The aged films performed well on the clay coated stock.

Table 9. Adhesion of Tape to OPV and Ink on Leneta 3B Substrate

Coalescent in Ink and OPV	**Fresh, 3 Hour Dry**		**After 3 Day Dry**	
	Rating	**Board Failure**	**Rating**	**Board Failure**
No Coalescent	2A	No	3A	No
X-613	4A	No	5A	No
DPM	5A	No	4A	No
C	5A	No	5A	No

Ratings = 5A is best and 1A poorest

Table 10. Adhesion of Tape to OPV and Ink on Clay Coated Board Substrate

Coalescent in Ink and OPV	**Fresh, 3 Hour Dry**		**3 Day Dry**	
	Rating	**Board Failure**	**Rating**	**Board Failure**
No Coalescent	2A	Yes	1A	Yes
X-613	2A	Yes	3A	Yes
DPM	3A	Yes	2A	Yes
C	1A	Yes	2A	Yes

Table 11. Adhesion of Tape to OPV and Ink on Oxidized Polypropylene Substrate

Coalescent in Ink and OPV	**Fresh, 3 Hour Dry**	
	Rating	**Board Failure**
No Coalescent	0B	No
X-613	3B	No
DPM	2B	No
C	2B	No

Rating = 5B is best and 0B poorest

[0157] Color Density

[0158] The Dc obtained for the inks did not vary much. They ranged from 1.23 to 1.28 for the evaluation of OPV over ink.

[0159] The foregoing examples illustrate basic screens for use of low VOC coalescent/plasticizers in binary blends, OPV's and inks. The inventive dibenzoate, X-

613, has demonstrated that it is an excellent lower VOC plasticizer/coalescent. It is also a non-phthalate and a non-ether.

[0160] Of the control coalescents tested, it would appear that the traditionally used TMPDMB is not a good choice for these types of OPV's and waterborne inks as it had limited compatibility with the base polymer that was used. The BCL and C were also limited in compatibility and utility.

[0161] Examples 5 and 6 – *Paint Evaluations*

[0162] Experimental Methodology

[0163] Coatings Tested:

[0164] A semi-gloss acrylic (Rhoplex™ SG-30) and a vinyl acrylic flat paint (UCAR® 379 G) were tested.

[0165] Listed below are the key parameters of the coatings:

Vinyl acrylic flat paint – Volume solids = 34.8% and PVC = 58%
Acrylic semigloss – Volume solids = 33.7% and PVC = 29.8%

[0166] The following coalescent/plasticizers were evaluated:

TMPDMB – 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate
TEGDO – Triethylene glycol di-2-ethyl hexanoate
X-613 – the inventive monobenzoate, 3-PPB

[0167] Paint/Coating Testing. The paint evaluations consisted of the following determinations:

[0168] Physical Properties, including WPG, pH, gloss, and Hide.

[0169] Performance Properties, such as block resistance, scrub resistance, dry-time, open-time/wet edge, heat age stability, low temperature touch-up, low temperature porosity, mudcrack resistance and freeze-thaw stability.

[0170] Details of the test methods are listed in Table 12, below:

Table 12. Summary of Test Methods Employed

Test	**Reference/method**
Blocking Resistance	ASTM D4946 – 3 mil wet films applied to Leneta WB chart and the films were dried for 7 days. Blocking was tested face to face at ambient and 120°F with a 1 Kg weight in place. The samples were separated and rated.
Dry Adhesion	ASTM D3359B – Paint was applied to dried aged alkyd with a brush and dried for 7 days before testing by cross hatch tape adhesion.
Drying Time	ASTM D1640 – 3 mil wet film applied to Leneta 3B, set to touch determined at ambient.
Flow & Leveling	ASTM D4062 – Leneta test blade used to apply paint. Dried paint rated.
Freeze/Thaw	ASTM D2243 – Frozen at 0°C and thawed at ambient. 3 cycles used.
Gloss and Sheen	ASTM D2243 – 3 mil wet film on Leneta 3B chart dried for five days.
Heat Stability	ASTM D1849 – Tested at 120°F for two weeks. Initial and final viscosities taken.
ICI Viscosity	ASTM D4287
Low Temperature Coalescence	Paint and equipment conditioned at 40°F for 2 hours. Paint drawn down on a Leneta Form HK to 6 mils wet. The films were dried horizontal for 24 hours and rated (lab rating 10= excellent, 0= very poor).
Mudcracking	Paint was applied with a Leneta Antisag meter (14-60 mils) on an HK chart at ambient and 40°F. After 24 hour dry the greatest mils without cracking noted.
pH	ASTM E70
Sag Resistance	ASTM D4400
Scrubbability	ASTM D2486 – Paint applied at 7 mils wet to a Leneta P121-10N chart and dried at room temperature for 7 days. A 10 shim was employed with abrasive media (SC-2). Failure was a continuous thin line at the shim.
Stormer Viscosity	ASTM D562
Touch Up	Touch up was tested with the paint prepared for the color acceptance. Self-primed Upsom was used and applied with a Linzer 2"Bristle and polyester brush at RT and 40°F and allowed to dry overnight. The test paint was applied and rated for sheen uniformity and color difference.
Wet Edge/Open Time	Paint applied with notched drawdown bar on Leneta WB chart. At 1 minute intervals ¼ of 1" brush was dipped into the paint and brushed 10 strokes across the line. The wet edge was rated with the lab system.
WPG	ASTM D1475

[0171] Example 5 – *Semigloss Acrylic*

[0172] Table 13 below shows the physical property determinations for the semigloss acrylic using the above noted plasticizers/coalescents and a blank.

Table 13. Physical Properties, Semigloss Acrylic

	TMPDMB	TEGDO	X-613	Blank
WPG	10.46	10.46	10.46	10.47
pH	8.5	8.4	8.9	8.7
Gloss 20°	44	51	53	44
Gloss 60°	80	83	83	79
Gloss 85°	96	96	95	96

[0173] The results show equivalent performance for 3-PPB as compared to several coalescents, including an industry standard coalescent and one claimed to have low VOC content (TEGDO).

[0174] Table 14 below shows the rheology results of the semigloss acrylic for the various plasticizers/coalescents evaluated.

Table 14. Rheology, Semigloss Acrylic

	TMPDMB	TEGDO	X-613	Blank
Stormer Viscosity (KU)	119	122	121	109
ICI	2.1	2.0	2.2	2.1
Level	6	6	6	7
Sag Resistance	24	24	24	24

[0175] Again, the results show that 3-PPB had equivalent performance.

Table 15. HIDE, Semigloss Acrylic

	TMPDMB	TEGDO	X-613	Blank
Contrast Ratio	98	98	98	98
Reflectance	94	92	93	94

[0176] Table 15 shows the HIDE results of the semigloss acrylic. HIDE results reflect the ability of the coating to cover the substrate completely.

[0177] Figure 11 reflects block resistance results of the semigloss acrylic at 1-day (RT and 120°F) for the evaluated plasticizers/coalescents. 3-PPB performed very well in this test, with no real differences between the samples tested. 3-PPB is a lower VOC content plasticizer/coalescent than TMPDMB, but higher than TEGDO. These block resistance results are important, because they counter the paradigm that a plasticizer, which is thought to have high permanence (lower volatility) than a volatile material, will soften and therefore have poor blocking, as well as other characteristics, such as lower Konig hardness. This data proves that the paradigm is false when it comes to the benzoate family of plasticizers.

[0178] Figure 12 shows block resistance results of the semigloss acrylic at 7-day (RT and 120°F) for the evaluated plasticizers/coalescents. 3-PPB demonstrated excellent performance, much better than TMPDMB and TEGDO.

[0179] Figure 13 shows the scrub resistance results of the semigloss acrylic for the plasticizers/coalescents evaluated. Results show that 3-PPB performed very well, at least as good as TMPDMB, the industry standard, and slightly better than TEGDO.

[0180] Table 16 below shows the dry time in minutes of the semigloss acrylic for the evaluated plasticizers/acrylics. While faster is good, that must be balanced against open time. Results show that 3-PPB performed similarly to the other evaluated plasticizers/coalescents.

Table 16. Dry Time, Semigloss Acrylic

	TMPDMB	TEGDO	X-613	Blank
Dry Time (minutes)	8	9	10	9

[0181] Figure 14 shows open-time, wet edge for the semigloss acrylic for the plasticizers/coalescents evaluated. The results show that 3-PPB performs at least as good as the other plasticizer/coalescents and in some instances better.

[0182] Figures 15 (a) and (b) show heat age stability results, both Delta viscosity and Delta E, color shift, respectively, of the semigloss acrylic for the plasticizers/coalescents evaluated. Not a lot of difference was perceived between the various plasticizer/coalescents in terms of viscosity changes or Delta E.

[0183] Figure 16 shows the mudcrack resistance results of the semigloss acrylic for the plasticizers/coalescents evaluated. Results were reported for ambient sealed, ambient unsealed, 40° F sealed and 40° F unsealed. There were no basic differences between any of the plasticizers/coalescents evaluated.

[0184] Table 17 below shows the low temperature film formation/porosity results of the semigloss acrylic for the plasticizers/coalescents evaluated. The results show a performance advantage for 3-PPB.

Table 17. Low Temperature Film Formation/Porosity, Semigloss Acrylic

	TMPDMB	TEGDO	X-613	Blank
Porosity Ratio	0.2	0.3	0.1	3.6

[0185] Figure 17 reflects the low temperature, touch-up results of the semigloss acrylic for the plasticizers/coalescents evaluated. Basically, there was no difference between the various plasticizers/coalescents evaluated, although TMPDMB and 3-PPB showed a slight advantage over TEGDO in color.

[0186] Freeze-thaw stability results of the semigloss acrylic showed freeze-thaw stability failure in all samples.

[0187] Example 6 – *Vinyl Acrylic Flat Paint*

[0188] Tables 18, 19 (rheology) and 20 (HIDE), below, show the physical properties of the vinyl acrylic flat paint for plasticizers/coalescents evaluated. The results show no differences among the various plasticizers/coalescents evaluated.

Table 18. Physical Properties, Vinyl Acrylic Flat

	TMPDMB	TEGDO	X-613	Blank
WPG	11.30	11.33	11.35	11.43
pH	8.87	8.85	8.91	8.85
Gloss 20°	1.1	1.1	1.1	1.1
Gloss 60°	1.8	1.8	1.9	1.8
Gloss 85°	1.2	1.2	1.4	1.2

Table 19. Rheology, Vinyl Acrylic Flat

	TMPDMB	TEGDO	X-613	Blank
Stormer Viscosity (KU)	89	90	89	97
ICI	1.1	1.1	1.2	1.2
Level	5	5	9	9
Sag Resistance	14	14	14	12

Table 20. HIDE, Vinyl Acrylic Flat

	TMPDMB	TEGDO	X-613	Blank
Contrast Ratio	89	87	87	89
Reflectance	88	88	88	89

[0189] Figure 18 shows the block resistance 7-day results (RT and 120°F) of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated. There were no differences between the plasticizers/coalescents evaluated.

[0190] Figure 19 shows the scrub resistance results of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated. There were no significant differences among the various plasticizers/coalescents.

[0191] Table 21 below reflects the dry time results of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated. While 3-PPB had a longer dry time, that may be an advantage for wet edge/open time results.

Table 21. Dry Time, Vinyl Acrylic Flat

	TMPDMB	TEGDO	X-613	Blank
Dry time (minutes)	11	12	14	11

[0192] Figure 20 shows the open-time/wet-edge results of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated. There may be some wet edge advantages with 3-PPB over time.

[0193] Figures 21 (a) and (b) show the heat age stability, both Delta viscosity and Delta E, color shift results, respectively, of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated. Results show that 3-PPB performed comparable to the other plasticizers/coalescents.

[0194] Figure 22 shows the mudcrack resistance results of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated. Results were obtained ambient-sealed; ambient-unsealed; 40° F-sealed, and 40° F-unsealed. Results showed that all the plasticizers/coalescents were equivalent.

[0195] Table 22 shows the low temperature film formation/porosity results of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated. Results show that all the plasticizers/coalescents performed better than the blank. 3-PPB performed well, but not quite as good as the other samples, indicating that it was not as efficient in film formation in vinyl acrylic flat paint.

Table 22. Low Temperature Film Formation/Porosity, Vinyl Acrylic Flat

	TMPDMB	TEGDO	X-613	Blank
Porosity Ratio	1.4	2.1	2.3	3.0

[0196] Figure 23 shows the low temperature touch-up results of the vinyl acrylic flat paint for the plasticizers/coalescents evaluated. Results show similar performance across the board.

[0197] Freeze-thaw stability results for the vinyl acrylic flat paint showed freeze-thaw stability failure in all samples.

[0198] The foregoing results demonstrate that 3-PPB is a viable low VOC alternative for use as a plasticizer/coalescent in polymeric coating applications.

[0199] In accordance with the patent statutes, the best mode and preferred embodiments have been set forth; the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

[0200] Any reference to background art herein is not to be construed as an admission that such art constitutes common general knowledge in Australia or elsewhere.

[0201] In the claims which follow and in the preceding description of the invention, except where the context clearly requires otherwise due to express language or necessary implication, the word “comprise”, or variations thereof including “comprises” or “comprising”, is used in an inclusive sense, that is, to specify the presence of the stated integers but without precluding the presence or addition of further integers in one or more embodiments of the invention.

WHAT IS CLAIMED IS:

1. A monobenzoate when used as a lower VOC plasticizer/coalescent in paint and other polymer-based coatings, comprising: 3-phenyl propyl benzoate.

2. A polymer-based coatings composition comprising a plasticizer that is 3-phenyl propyl benzoate, wherein the 3-phenyl propyl benzoate imparts comparable or better film formation, gloss, hardness, water resistance, block resistance, and scrub resistance as compared to that obtained with a traditional plasticizer/coalescent.

3. An acrylic paint formulation, comprising a plasticizer/coalescent that is 3-phenyl propyl benzoate.

4. A monobenzoate coalescent when used in waterborne overprint varnishes and inks, comprising: 3-phenyl propyl benzoate.

5. An overprint varnish composition, comprising a polymeric dispersion and a coalescent that is 3-phenyl propyl benzoate.

6. A waterborne overprint varnish composition, comprising:

a. a polymeric dispersion; and

b. a low VOC coalescent that is 3-phenyl propyl benzoate present in amounts ranging from about 2% to about 8% wet.

7. The composition as set forth in claims 5 or 6, wherein the polymeric dispersion comprises a styrenated acrylic polymer:

8. A waterborne ink composition comprising a polymeric dispersion and a low VOC coalescent that is 3-phenyl propyl benzoate.

9. A waterborne ink composition, comprising

   a. a polymeric dispersion
   b. a low VOC coalescent that is 3-phenyl propyl benzoate; and
   c. a pigment,

   wherein the coalescent is present in amounts ranging from about 2% to about 8% wet,

10. The composition as set forth in claims 8 or 9, wherein the polymeric dispersion comprises a styrenated acrylic polymer.

11. A monobenzoate plasticizer/coalescent when used in waterborne polymer compositions comprising polyvinyl acetates, vinyl acetate ethylene, vinyl acrylates, methacrylates, styrene acrylates, polyurethanes, vinyl chloride co- and ter-polymers, vinyl esters of versatic acid, or mixtures thereof, wherein the monobenzoate is 3-PPB.

12. A monobenzoate plasticizer/coalescent when used in non-aqueous based polymer compositions comprising acrylics, polyvinyl acetate, vinyl acetate ethylene, methacrylates, styrene acrylates, epoxies, polyamides, nitrocellulose, vinyl chloride or mixtures thereof, wherein the monobenzoate is 3-PPB.

13. A blend of plasticizers/coalescents when used in polymeric coatings comprising 3-PPB combined with phthalates up to C5, terephthalates up to C4, phosphate esters, polyesters, citrates, isobutyrates, sulfonamides, sulfonic acid esters, epoxy plasticizers, benzoate esters or mixtures thereof.

14. A blend of plasticizers/coalescents when used in polymeric coating compositions comprising 3-PPB combined with solid plasticizers that are sucrose benzoate, dicyclohexyl phthalate, triphenyl phosphate, glycerol tribenzoate, 1,4-cyclohexane dimethanol (CHDM) dibenzoate, pentaerythritol tetrabenzoate, alkyl glycol esters, or mixtures thereof.

15. A nail polish composition, comprising a polymeric dispersion and 3-PPB.

16. A method of improving the film formation properties of paints, overprint varnishes, inks and other coatings, comprising the step of adding 3-phenyl propyl benzoate alone or in combination with other plasticizers.

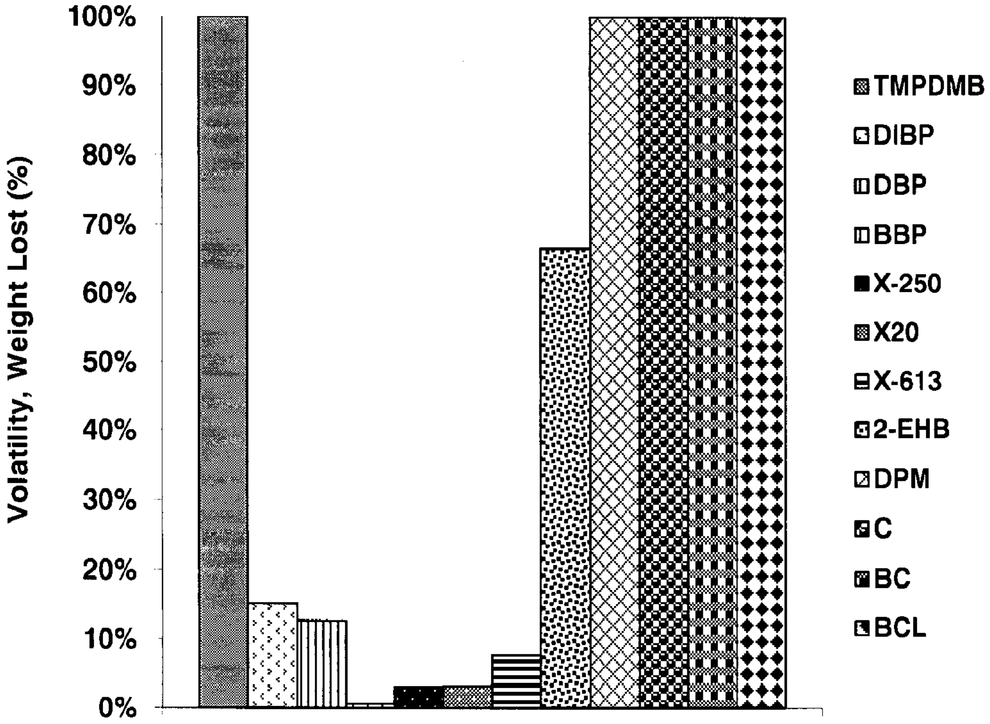

FIG. 1 ASTM D2369, 110°C for One Hour

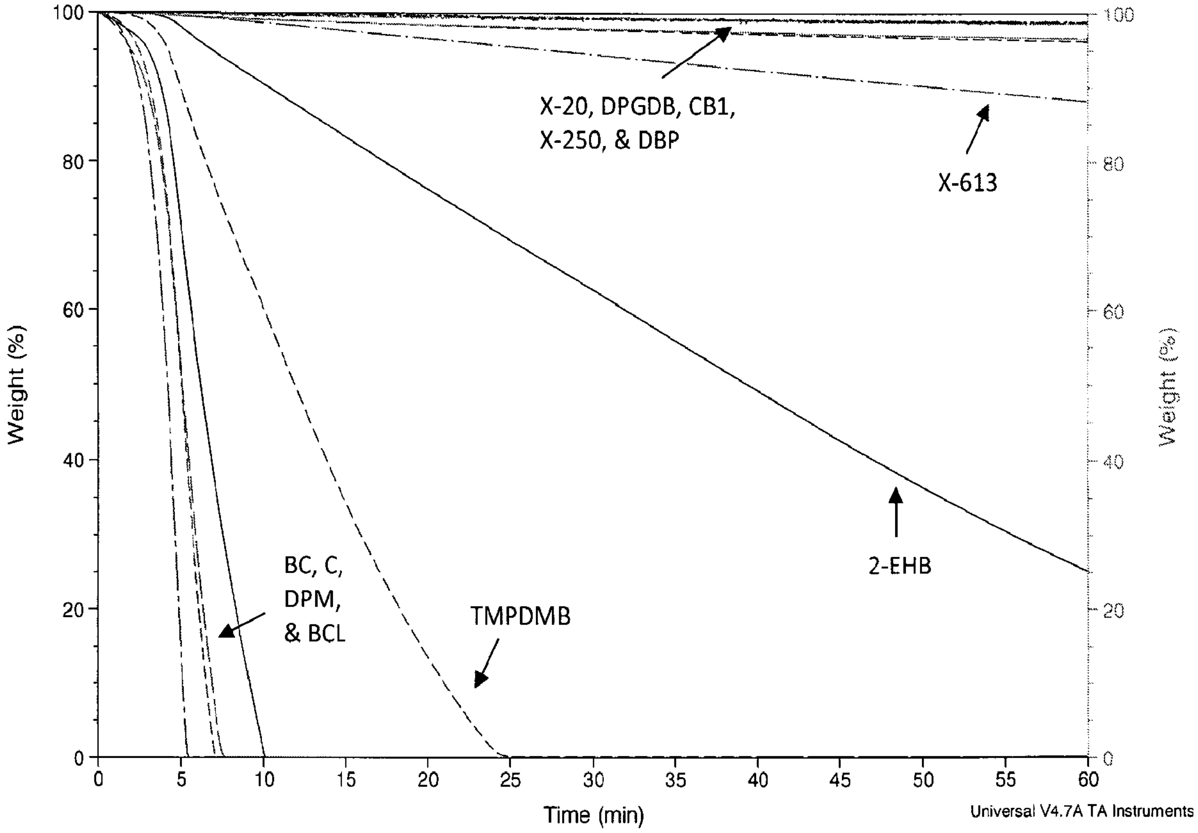

FIG. 2 TGA Isothermal Scan at 110°C for One Hour

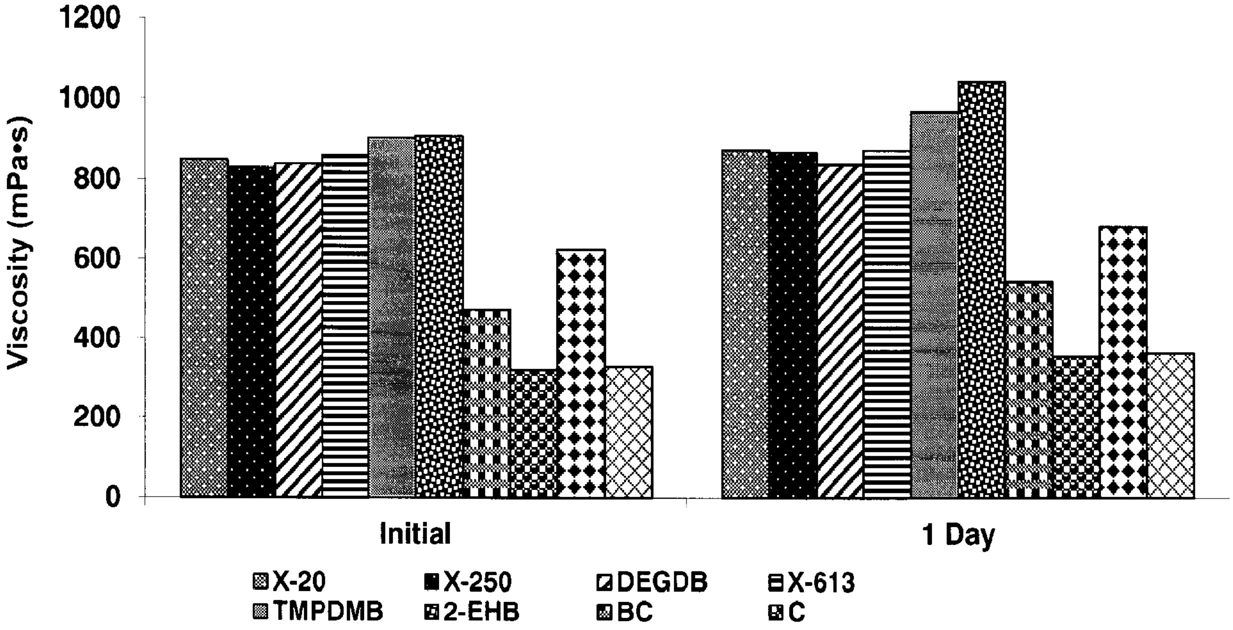

FIG. 3 Viscosity Response Data

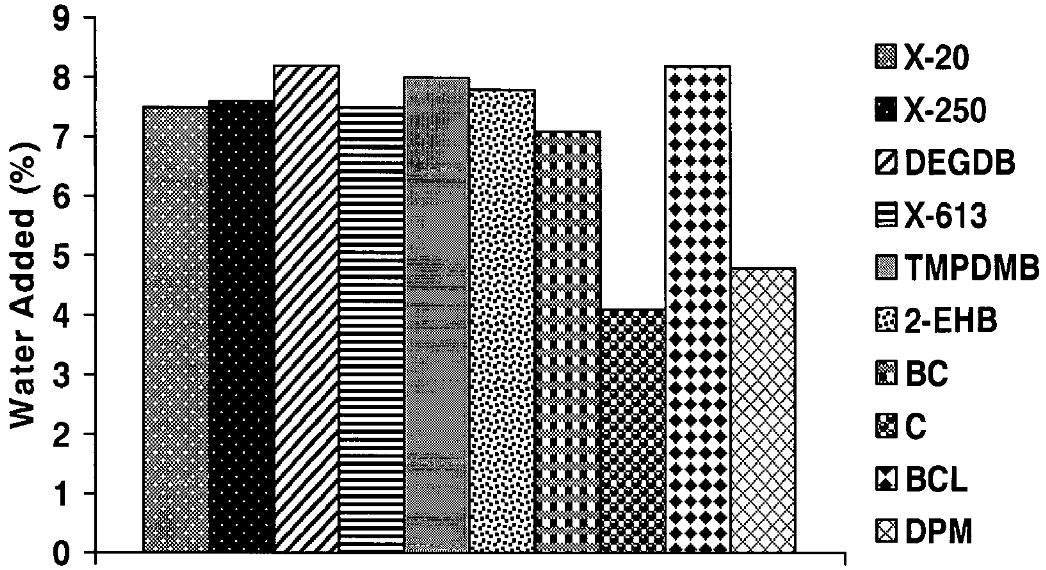

FIG. 4 Viscosity Reductions, Percent Water to 150 mPa·s

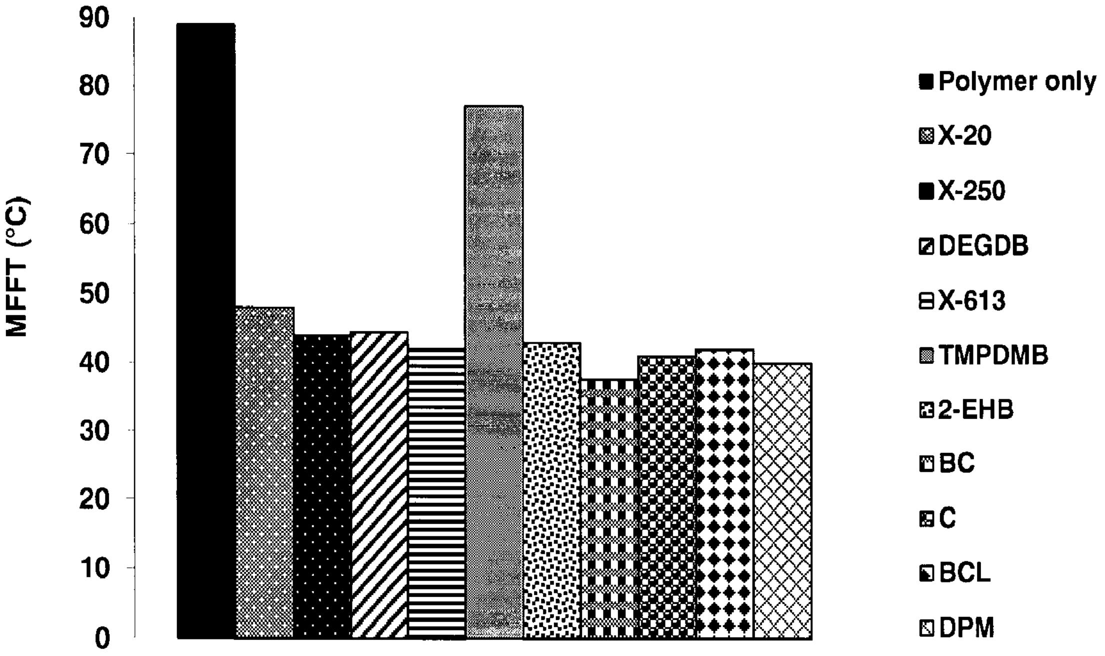

FIG. 5 MFFT Data on Binary Blends, 4% Plasticizer

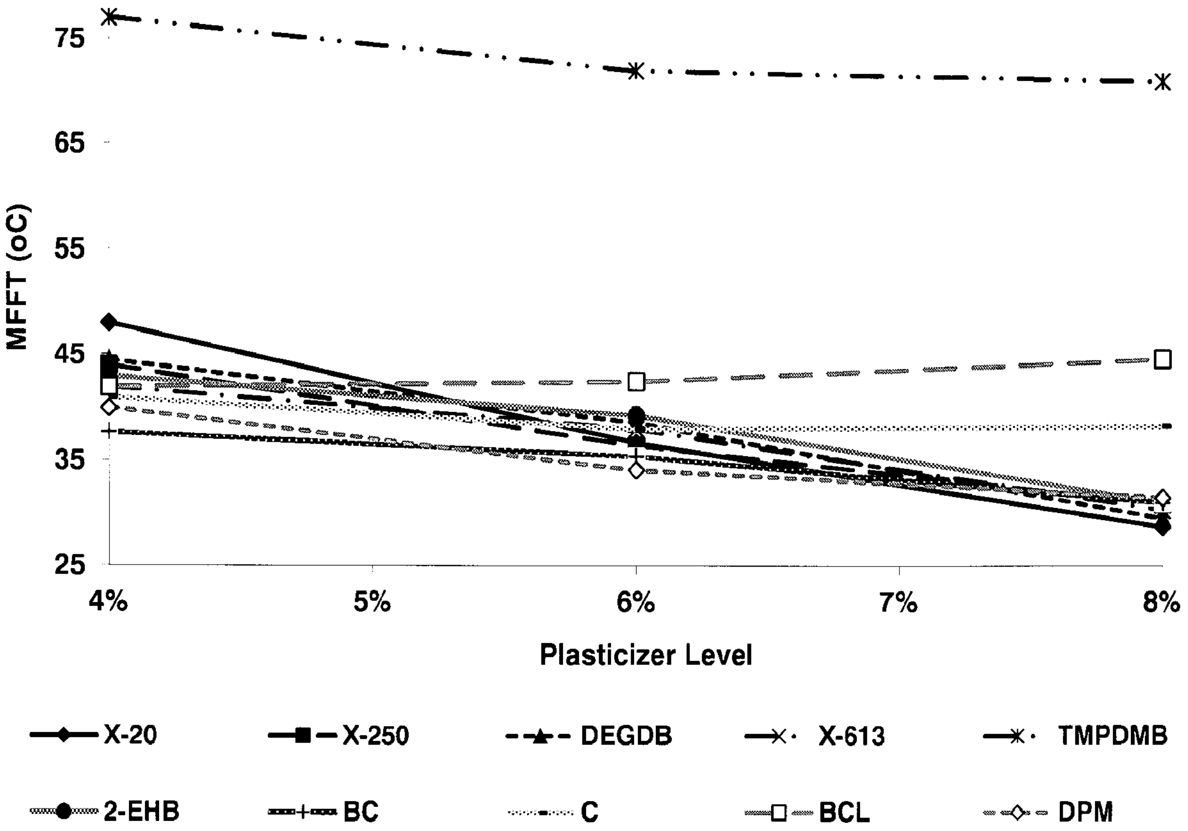

FIG. 6 MFFT Versus Plasticizer Level in Binary Blends

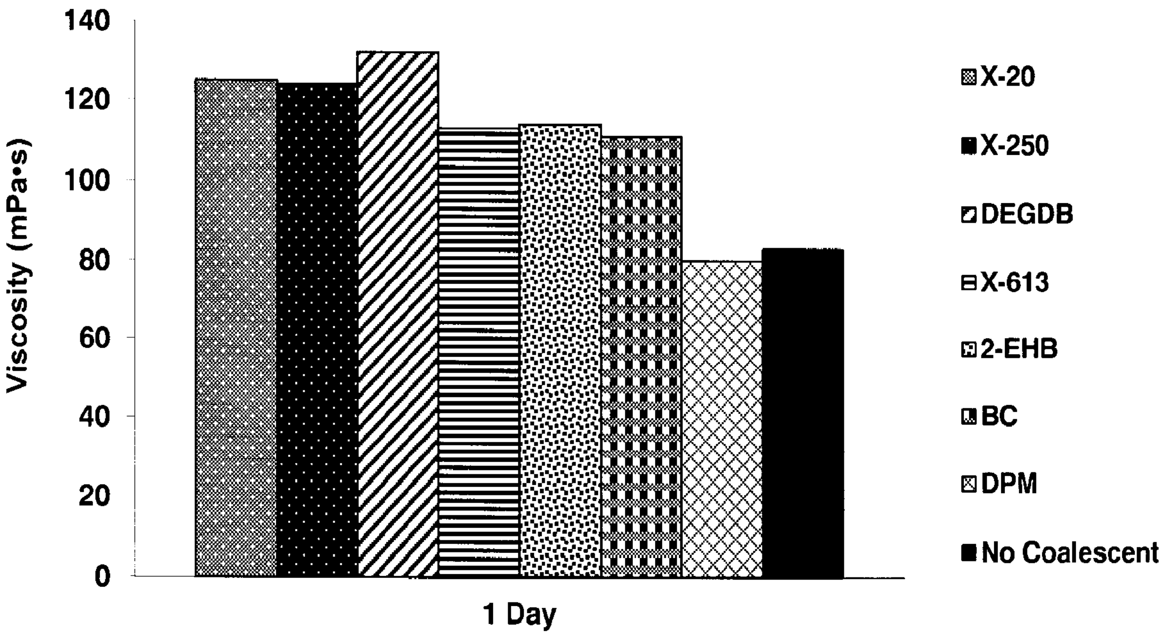

FIG. 7 OPV Viscosities, 1 Day Aging, 4% Coalescent

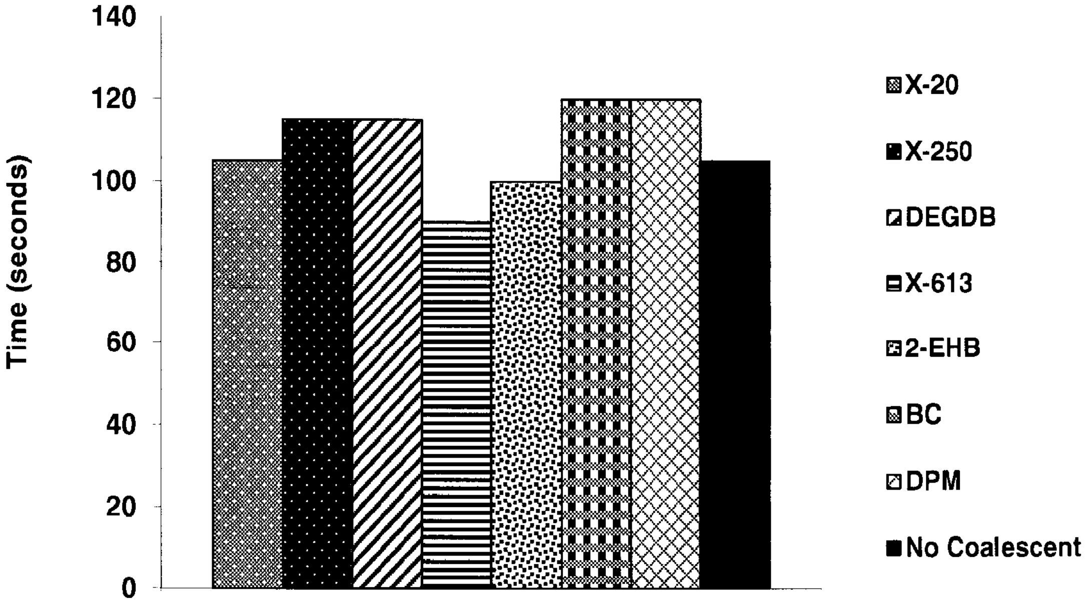

FIG. 8 Time to Dry to Touch

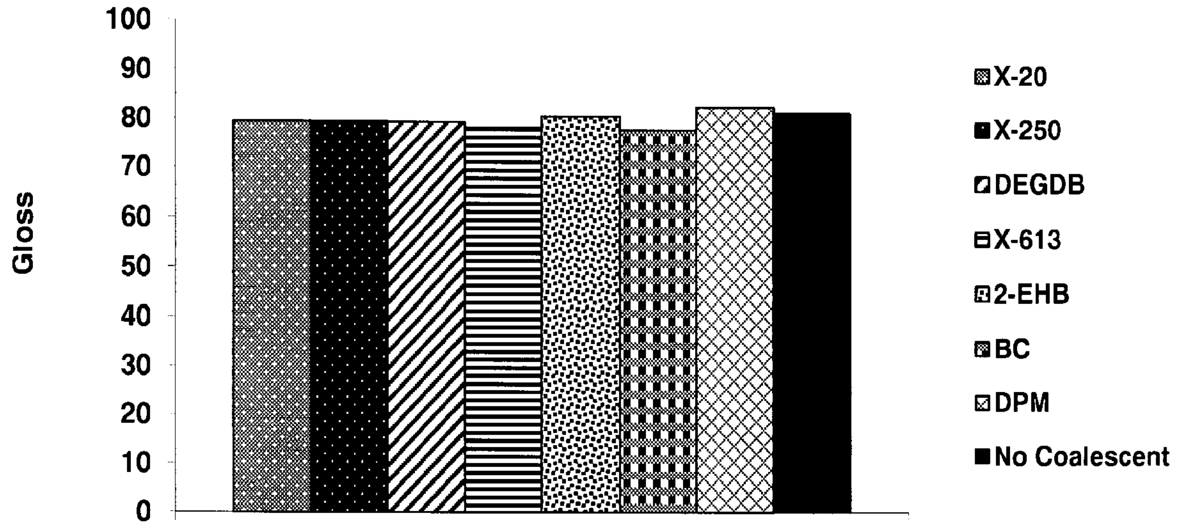

FIG. 9 20° Gloss – Leneta 3B Substrate

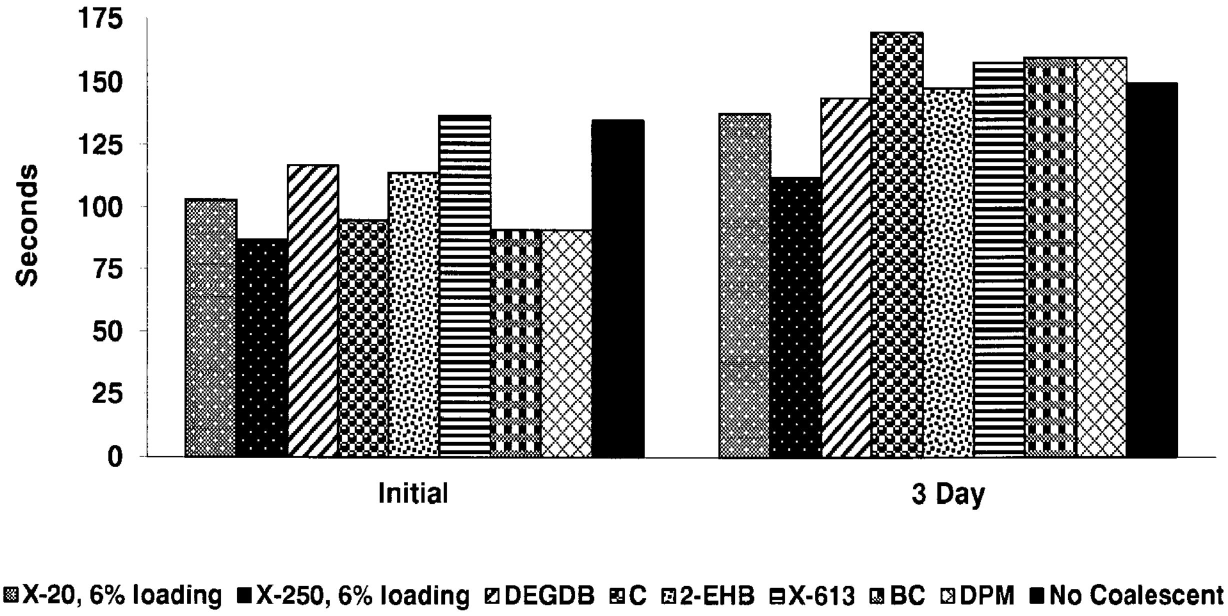

FIG. 10 Konig Hardness

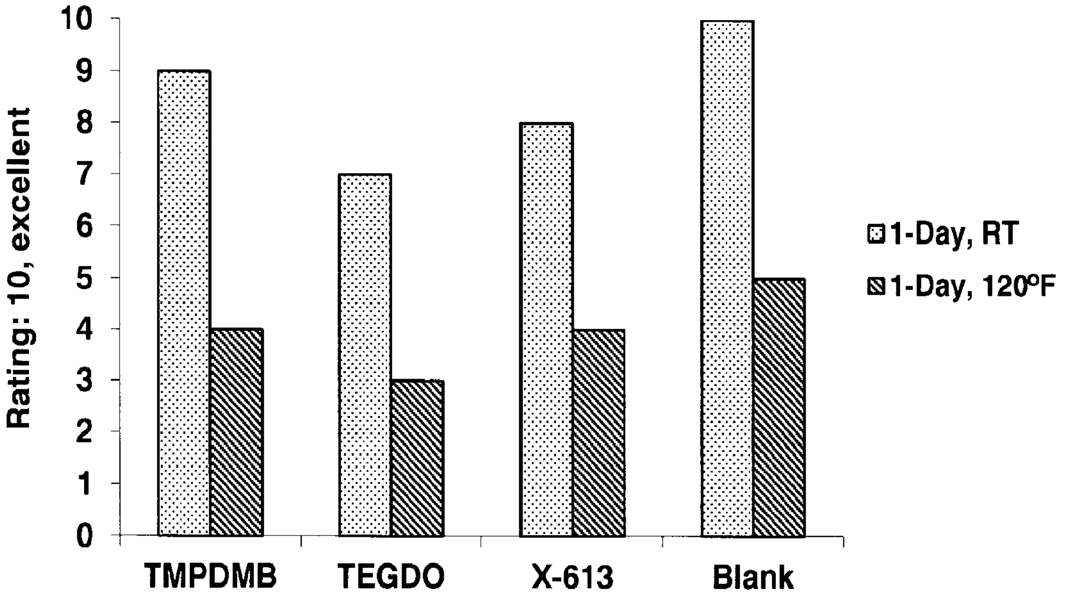

FIG. 11 Block Resistance, Semigloss Acrylic, 1-Day

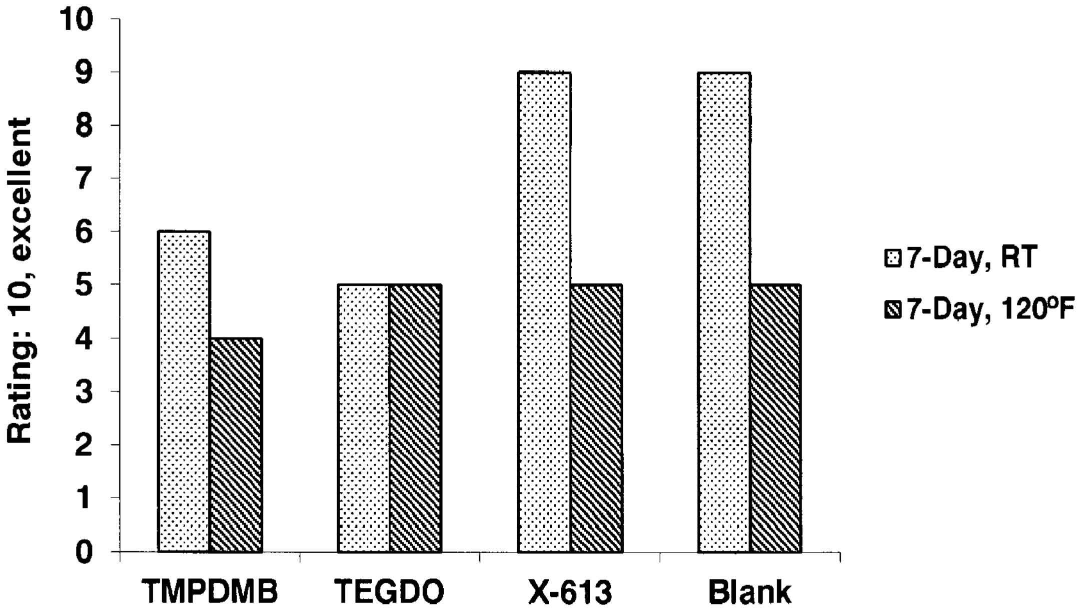

FIG. 12 Block Resistance, Semigloss Acrylic, 7-Day

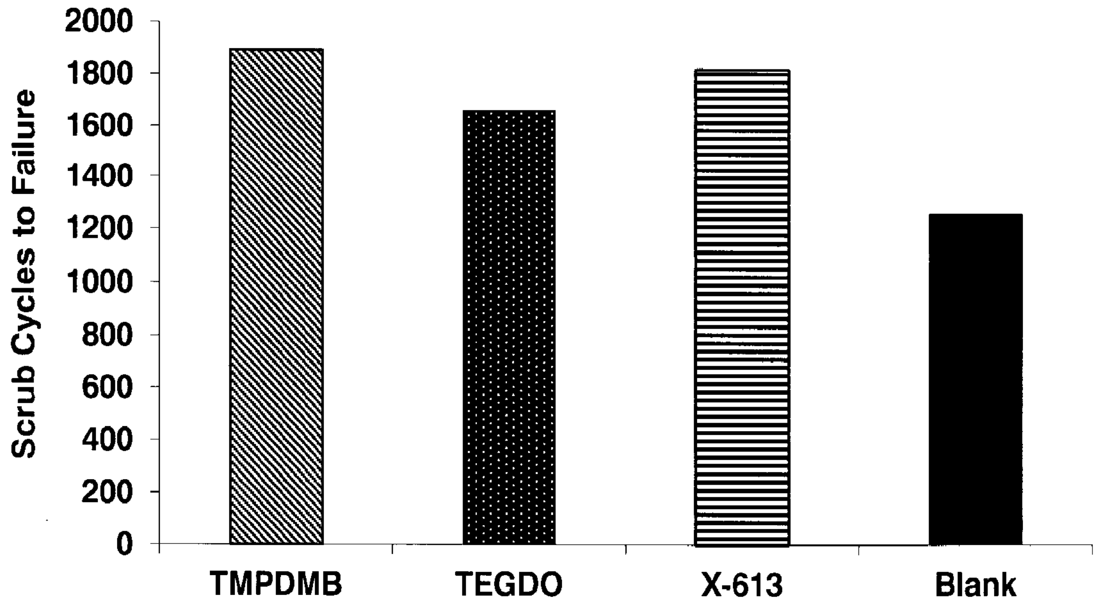

FIG. 13 Scrub Resistance, Semigloss Acrylic

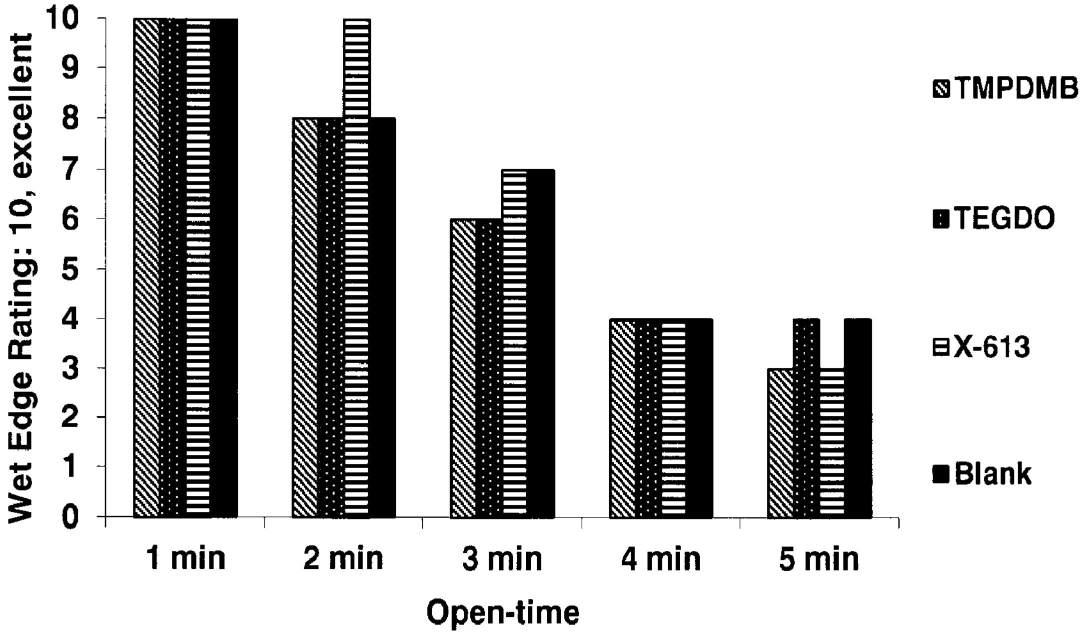

FIG. 14 Open-Time, Wet Edge, Semigloss Acrylic

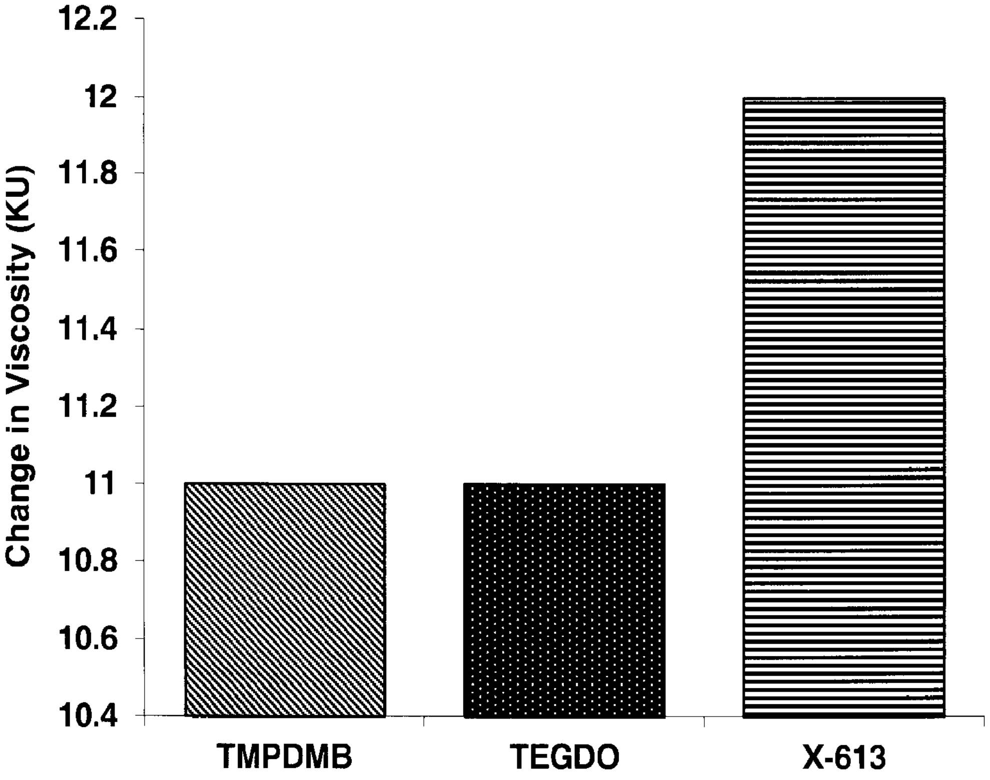

FIG. 15 a Delta Viscosity, Semigloss Acrylic

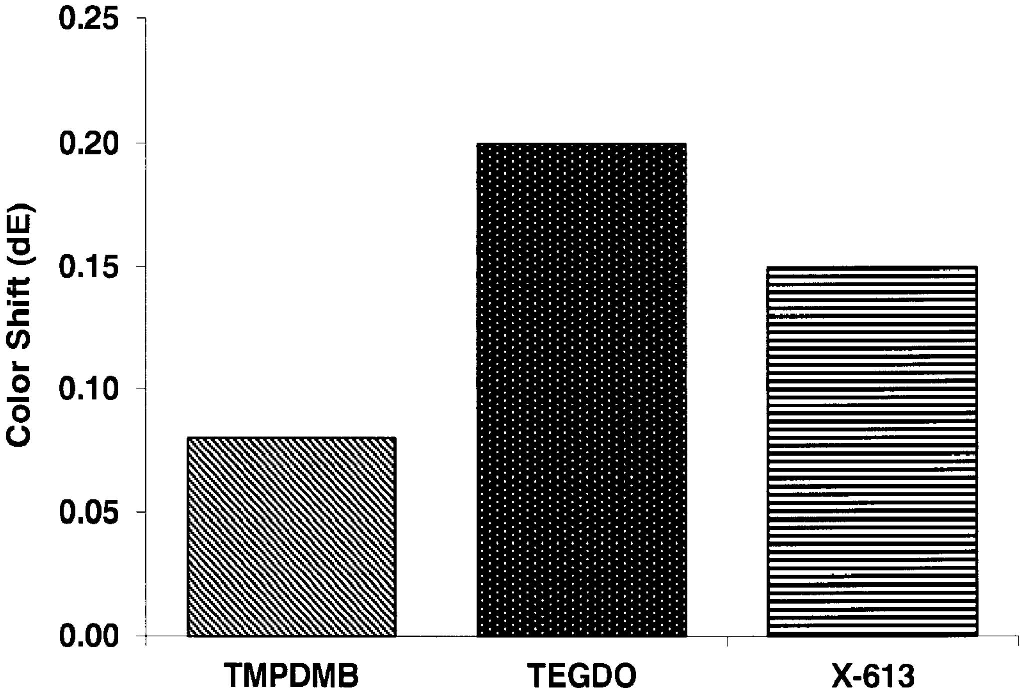

FIG. 15 b Delta E, Color Shift, Semigloss Acrylic

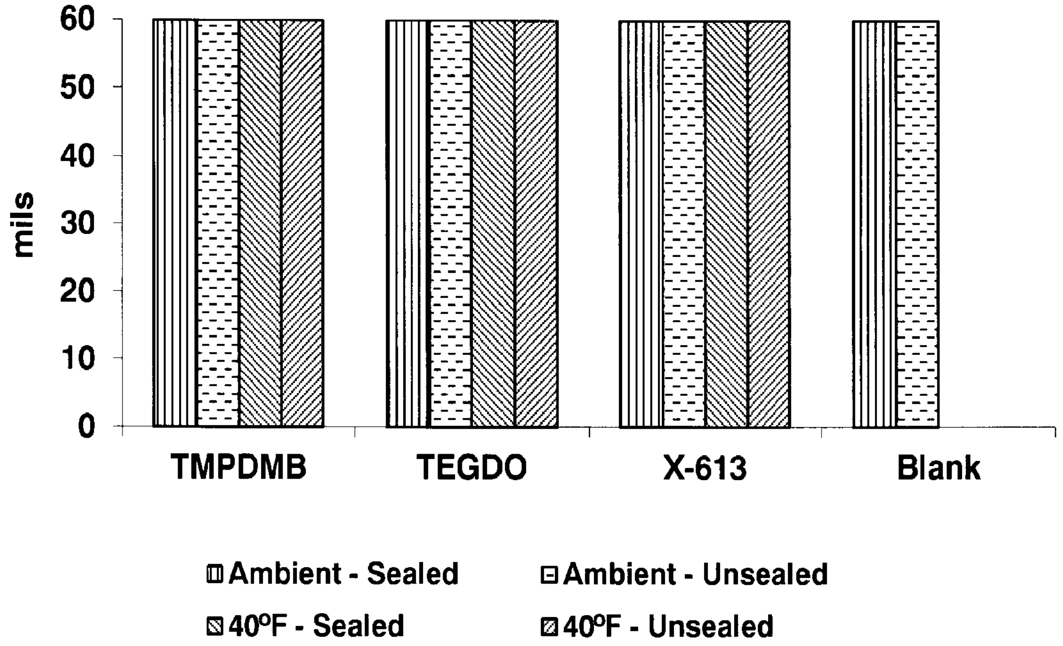

FIG. 16 Mudcrack Resistance, Semigloss Acrylic

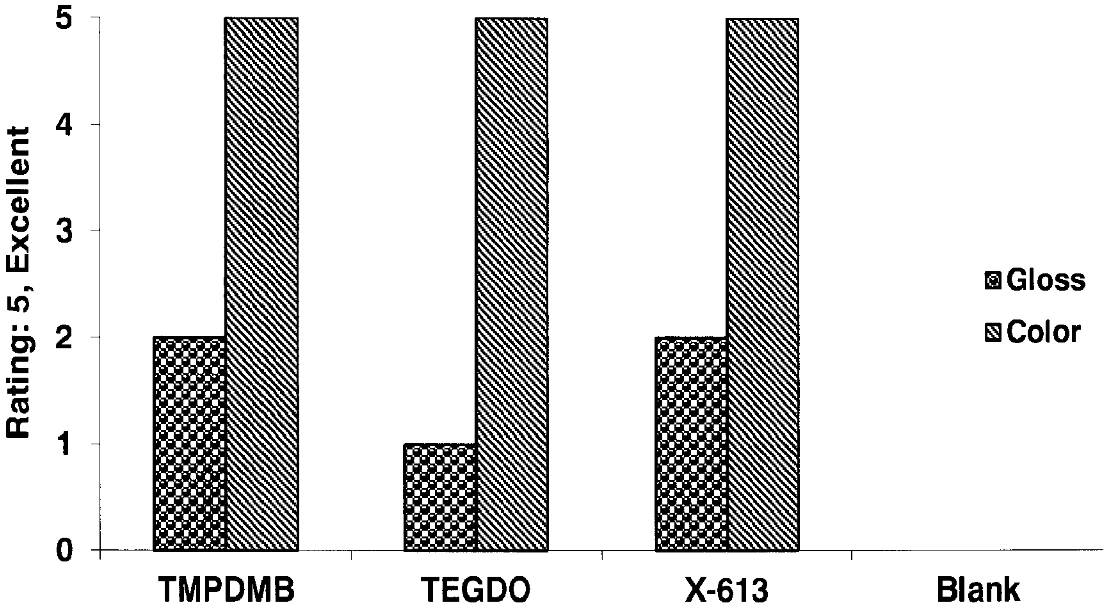

FIG. 17 Low Temperature Touch-Up, Semigloss Acrylic

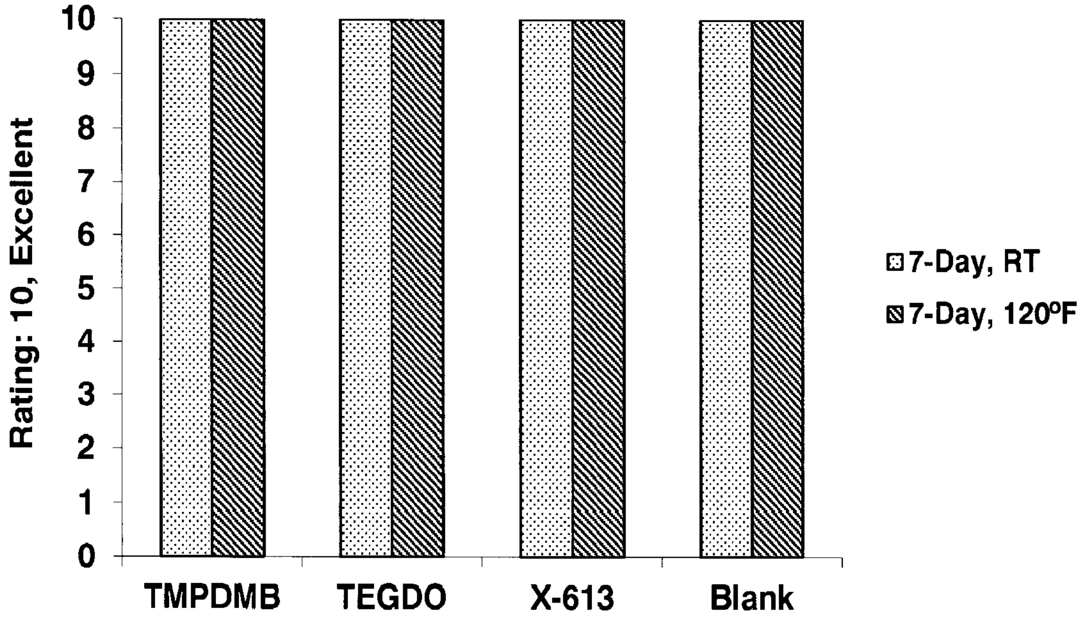

FIG. 18 Block Resistance, Vinyl Acrylic Flat, 7-Day

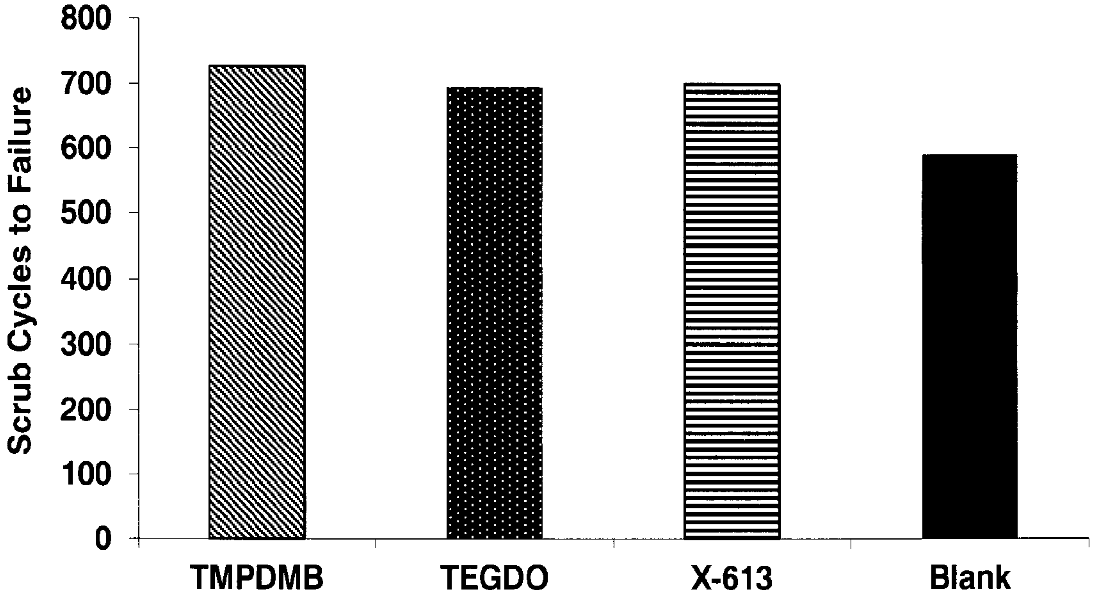

FIG. 19 Scrub Resistance, Vinyl Acrylic Flat

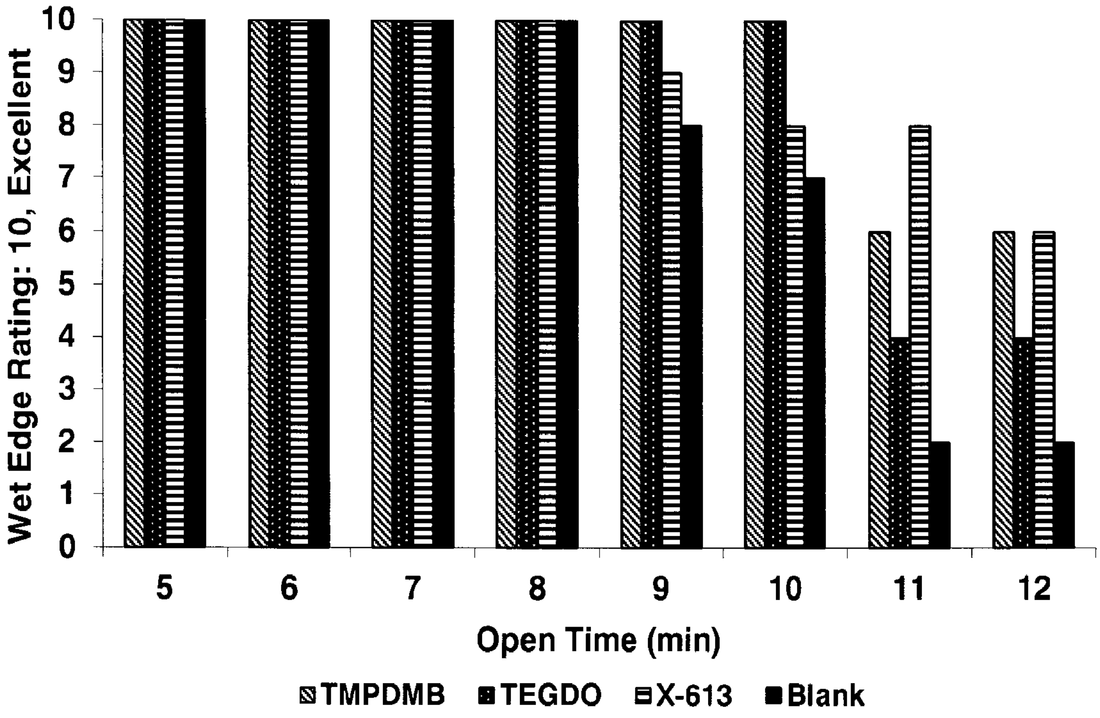

FIG. 20 Open-Time/Wet-Edge, Vinyl Acrylic Flat

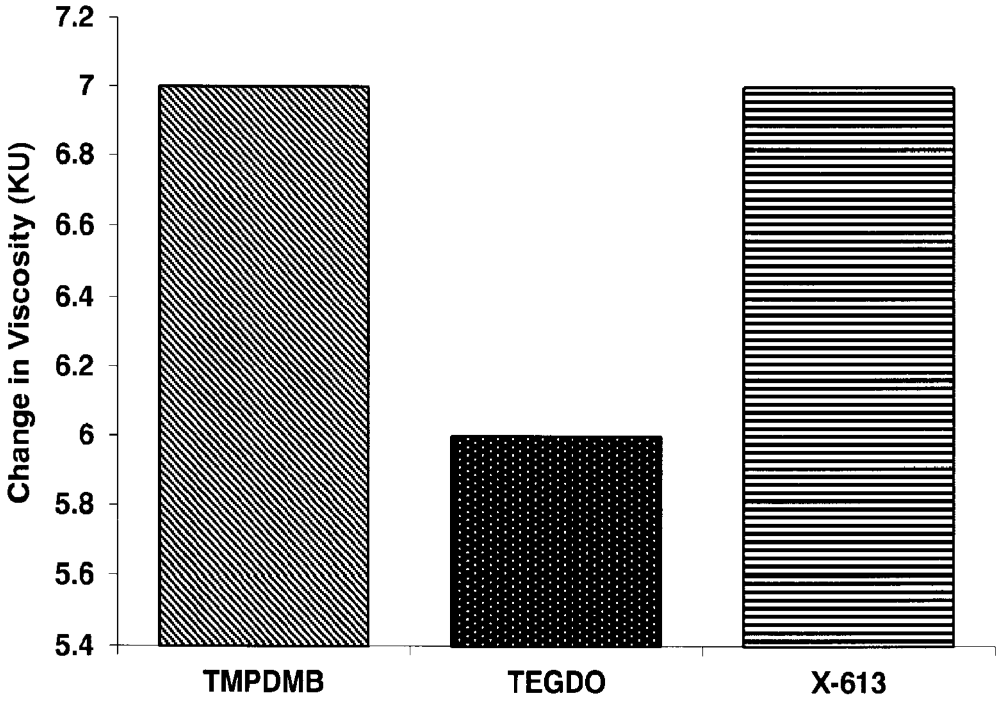

FIG. 21 a Delta Viscosity, Vinyl Acrylic Flat

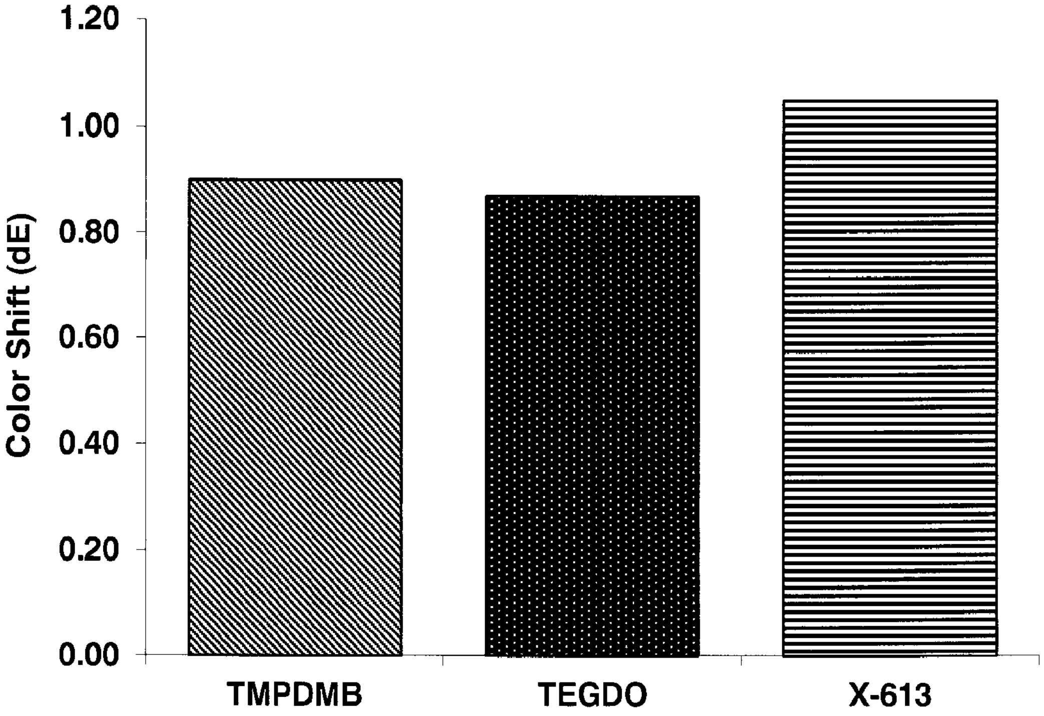

FIG. 21 b Delta E, Color Shift, Vinyl Acrylic Flat

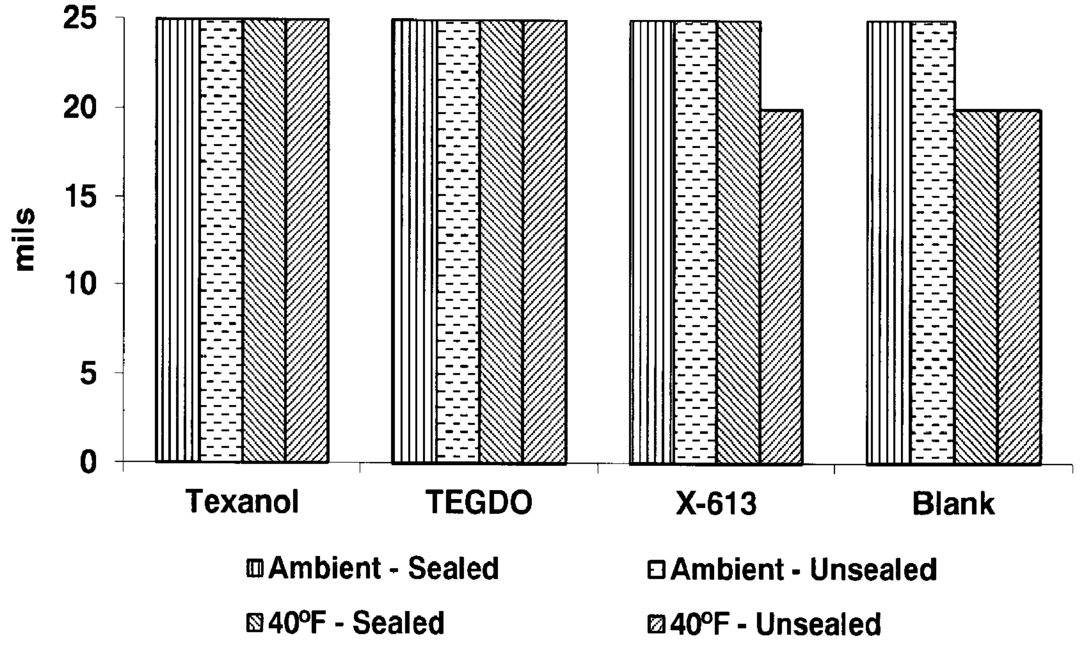

FIG. 22 Mudcrack Resistance, Vinyl Acrylic Flat

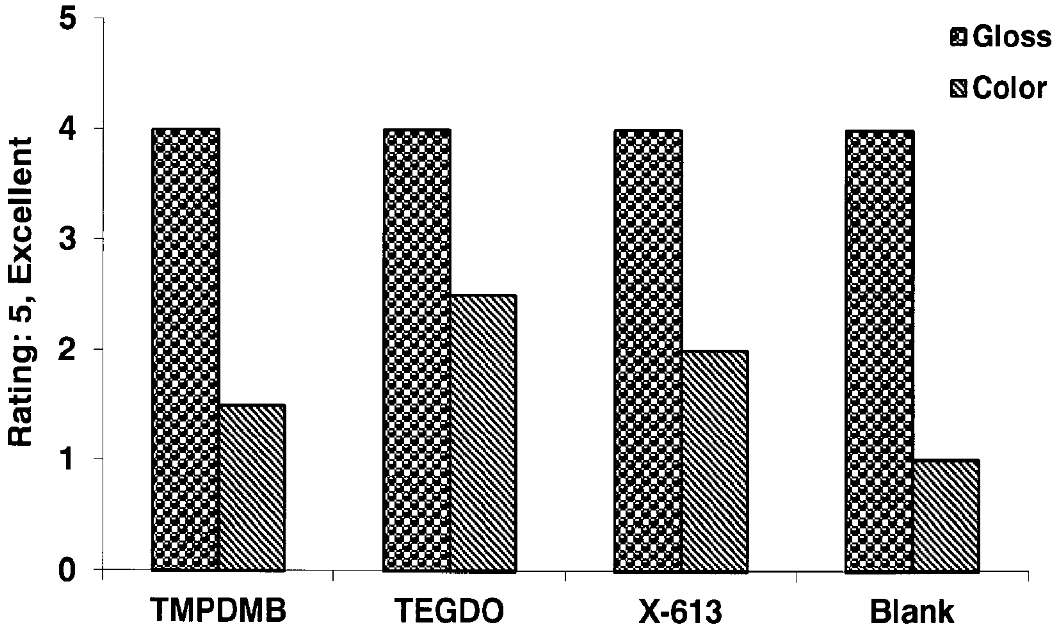

FIG. 23 Low Temperature Touch-Up, Vinyl Acrylic Flat