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— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

[Continued on next page]

(54) **Title:** LOW GHOSTING DRY ERASE ARTICLE AND USE THEREOF

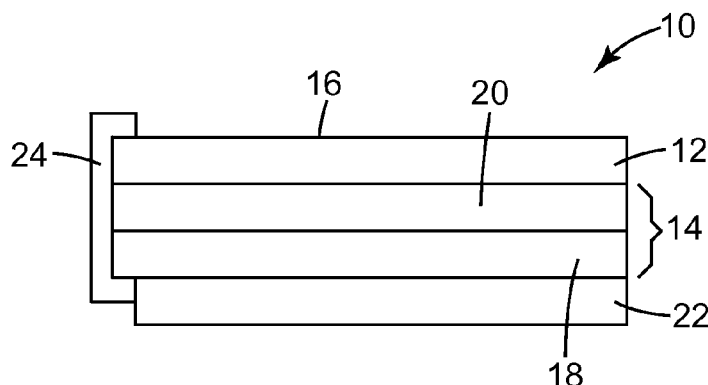


FIG. 1

(57) **Abstract:** Dry erase articles having a writing surface that exhibits good writing receptivity and good resistance to ghosting and method of using such articles.

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- Published:**
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LOW GHOSTING DRY ERASE ARTICLE
AND USE THEREOF

Field

5 This invention relates to a dry erase article having good writing receptivity to dry erase ink and easy removal of dry erase ink even after a long time between writing and erasing, and use of such articles.

Background

10 Dry erase boards have been used as writing surfaces for years because of their convenience and versatility. The boards provide a means for expression which eliminates the mess and trouble of a chalk board.

 Dry erase marker writing on a dry erase board should form a dark solid line without beading up. If dry erase ink beads up on the writing surface, it leaves broken lines or holes in the resultant written image. It is desirable to have a dry erase board on which
15 dry erase ink does not bead up.

 There are numerous dry erase articles in the marketplace. Illustrative writing surfaces on such articles include porcelain steel, melamine, painted metal, glass, and UV
 cured acrylate coatings. These surfaces can provide effective wet out of many
20 commercially available dry erase markers as well as adequate erasability if erased shortly after being written on, e.g., within a few hours. However, if left on the board for several days or weeks, the writing becomes increasingly difficult to erase with an eraser. The result is a remaining faint image of the writing, sometimes referred to as “ghosting”, that must be removed with a specialized liquid cleaner.

25 The need exists for dry erase writing surfaces that provide both good writing receptivity and good low ghosting properties.

Summary

 This invention provides a dry erase article with good writing receptivity, i.e., good
30 wet out of dry erase marker inks when writing thereon, and easy removal of dry erase markings with a dry eraser even after a long time between writing and erasing, i.e., low ghosting. It also provides methods of use that achieve heretofore unattained combination

of dry erase performance and ease of use, in some embodiments, novel high performance dry erase markers.

In brief summary, dry erase articles of the invention comprise having a writing surface that exhibits both good writing receptivity and good resistance to ghosting. Dry erase articles of the invention have writing surfaces with a wetting tension below about 38 mJ/m², typically below about 32 mJ/m², and in some embodiments from about 20 to about 30 mJ/m². Such wetting tension characteristics are below those of the writing surfaces of known commercial dry erase articles which are believed to have a wetting tension of at least about 38 mJ/m² or more.

The desired surface properties are achieved by applying a coating to the surface of writing member that yields a writing surface having desired properties or incorporating selected components in the writing member such that its front surface exhibits the desired properties.

Briefly summarizing, the method of the invention comprises:

- a) providing a dry erase article as described herein;
- b) writing first written matter on the writing surface using a dry erase marker comprising an ink having surface tension that is less than the surface energy of the writing surface; and
- c) erasing at least a portion of the first written matter with a dry eraser, typically with no more than 2, and preferably just 1, firm wipes by hand, such that the portion of written matter is no longer visible on the dry erase article.

In accordance with the invention, the method may be used to achieve low ghosting performance even with writing that is hours, days, or more old.

The invention also provides dry erase markers that, in brief summary, utilize fluid having significantly lower surface tension than the fluids used in conventional dry erase markers.

It has been discovered that the writing surfaces described herein provide surprising performance. Some of the advantages of dry erase articles of the invention include good writability coupled with good resistance to ghosting. Also, dry erase articles of the invention are more resistant to staining when marked with unsuitable writing instruments, e.g., so-called permanent markers rather than dry erase markers. A solvent such as isopropanol may be required to remove permanent markers from dry erase articles of the

invention, but writing with conventional dry erase markers can be removed by wiping with a conventional dry eraser for just one or two wipes. Moreover, dry erase articles of the invention typically exhibit excellent mechanical durability and resistance to yellowing with age.

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Brief Description of Drawing

The invention is further explained with reference to the drawing wherein:

Fig. 1 is a cross-sectional schematic of an illustrative embodiment of the invention.

This figure is not to scale and is intended to be merely illustrative and not limiting.

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Detailed Description of Illustrative Embodiments

For the following defined terms, these definitions shall be applied, unless a different definition is given in the claims or elsewhere in this specification.

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Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about". Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings of the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviations found in their respective testing measurements.

30

Weight percent, percent by weight, % by weight, and the like are synonyms that refer to the concentration of a substance as the weight of that substance divided by the weight of the composition and multiplied by 100.

The recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5). As used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a composition containing "a compound" includes a mixture of two or more compounds. As used in this specification and the appended claims, the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

Dry Erase Article Construction

An illustrative dry erase article of the invention is shown in Fig. 1 wherein dry erase article 10 comprising writing member 12 and optional backing member 14 is shown. In accordance with the present invention, front face 16 of writing member 12, i.e., the writing surface, exhibits both good writing receptivity and good resistance to ghosting. In some embodiments, backing member 14 comprises structural member 18 and optional primer layer 20 to achieve desired interply adhesion to writing member 12. In some embodiments, article 10 may further comprise optional adhesive 22 on its back side, e.g., shown here on the back side of backing member 14, adhesive 22 providing means to adhere article 10 to an adherend as desired. In some embodiments, article 10 may further comprise frame member 24 on one or more edge portions to secure the component members of article 10 together, facilitate handling of article 10, provide means of attaching article 10 to a supporting surface, etc.

Articles of the invention can be made in a variety of embodiments as desired, illustrative examples including, individual or padded sheets, e.g., similar to paper, films, adhesive-back labels, incorporated into folders, notebook covers, dry erase articles, etc.

Acceptance of ink on writing surface 16 as written indicia without beading of the ink can be defined as the "wettability" of the dry erase writing surface. Wettability refers to a writing line that can retain its shape and continuity as the solvent dries. Dewetting of solvent from the writing surface causes the line to move in or break at certain points, causing voids in the written matter. Acceptable wettability (or writing without dewetting) is typically accomplished if the surface energy of the writing surface is greater than the surface tension of the solvent component(s) in the marker ink. The wetting tension test method ASTM D 2578-08, Standard Testing Method for Wetting Tension of Polyethylene

and Polypropylene Films, is a direct measure of the wettability of a surface. In this test method, a liquid of known surface tension is applied to a surface. If the liquid does not bead up or dewet after 2 seconds, the liquid is said to wet the surface. The highest value surface tension liquid that does not bead up after 2 seconds is considered to be the wetting
5 tension of a surface.

Solvent compositions of dry erase markers are typically listed on the marker or reported on the MSDS for the marker. Common solvents for dry erase markers include, for example, ethanol, isopropanol, methyl isobutyl ketone and n-butyl acetate. One solvent with a high surface tension is n-butyl acetate, having a surface tension of about 25
10 mJ/m^2 . Therefore, in some embodiments, a dry erase surface can be wettable by solvents with a surface tension of about 25 mJ/m^2 or less. In one embodiment, the surface energy of the writing surface is within the range of about 26 mJ/m^2 to less than about 38 mJ/m^2 . In another embodiment, the surface energy of the writing surface is within the range of about 30 mJ/m^2 to less than about 38 mJ/m^2 .

The writing surface of articles of the invention additionally provides a level of "erasability" which allows the user to wipe away (e.g. with a dry cloth or dry eraser)
15 indicia written with a dry erase marker once it is no longer desired. Acceptable erasability is achieved if the surface energy of the writing surface is sufficiently low to prevent tenacious adhesion of the binders and other solids in the marker inks to the writing surface.
20 As used herein, good erasability is deemed to be substantially complete erasure of written matter with no more than 2, preferably only 1 wipe by hand with a dry eraser. One wipe of the eraser is defined as a single direction pass of the eraser over the writing surface. By hand is meant to imply a force of about 0.4 N/cm^2 . If lighter force is used, additional wipes may be required. The surprising erasability performance provided by writing
25 surfaces of the invention avoids the commonly encountered necessity of vigorous scrubbing action while erasing, making them easier to use by more people, and reducing the wear on erasers as well as the writing surfaces. Moreover, because easy erasability is achieved, users will not need to undertake to clean the writing surface with more powerful cleaning agents with objectionable odor and tools that might tend to degrade the writing
30 surface thereby shortening its surface life.

A variety of dry eraser types can be used in the present invention. Illustrative examples of eraser materials include pressed and woven felts of synthetic and/or natural

(e.g., wool) materials, cellulose, foam rubber, neoprene, cloth, pile fabrics, melamine fibers, and similar materials have been used. Preferably the eraser materials chosen is not abrasive in nature so as to enhance the durability of the writing surface.

5 The writing surface of the present invention also provides holdout of marker writing at the surface. Ghosting of dry erase writing can occur when the marker ink penetrates into the surface making it difficult or impossible to remove by simply wiping with a dry eraser. This penetration tends to occur if the writing surface is porous or soft. The present invention provides a writing surface that is not porous and is highly crosslinked to prevent ghosting due to penetration of the solvent into the writing surface.
10 As a result, writing surfaces of articles of the invention exhibit excellent resistance to ghosting.

Optional backing member 14 is selected to impart desired performance, e.g., color background to the writing surface, reflective properties in the case of dry erase articles with improved projection capability, etc.

15 In some embodiments, the dry erase article comprises a writing member 12 on one side of backing member 14 with an optional adhesive (not shown) on the second side of backing member 14 and an optional release liner (not shown) on the back of the adhesive.

In some embodiments, the dry erase article is a substrate with a cured coating on a portion of one side and an adhesive on a portion of the other side of the substrate, in which
20 the article is laminated to a second substrate which is then framed to make a dry erase board.

Writing Member

25 The advantageous benefits of the invention are attained with a writing member having a writing surface as described herein. The writing surface can be formed from a curable coating composition, e.g., by applying the composition to a substrate and curing or by forming a self-supporting cured film from the composition.

In a typical embodiment, the writing member comprises a coating or film formed from a radiation curable coating. The radiation curable coating incorporates acrylate
30 monomers and other polymerizable monomers or polymers and at least one polymerizable low surface energy monomer, oligomer, or polymer. This low surface energy monomer, oligomer, or polymer can be a fluorocarbon, silicone, or hydrocarbon. The low surface

energy monomer, oligomer, or polymer is added to the formulation in order to reduce the surface energy of the radiation cured coating, but still provide complete wet out of dry erase markers on the surface. After curing the surface coating has a wetting tension of from about 30 to less than about 38 mJ/m² as measured by ASTM D 2578-08.

5 In another embodiment, the invention comprises a radiation curable coating on a film or paper substrate with a wetting tension of from about 20 to about 30 mJ/m², referred to herein as "super low wetting tension" dry erase articles. An advantage of such "super low wetting tension" dry erase articles is that permanent markers will dewet or bead up, signaling to the user that the wrong markers were used. However, commercially
10 available dry erase markers do not effectively wet out such writing surfaces, instead they bead up to form voids in the writing. Thus, one aspect of this invention is to provide dry erase markers that wet out on "super low wetting tension" surfaces with wetting tension of from about 20 to about 30 mJ/m². Wet out on such writing surfaces can be achieved by reformulating marker ink to lower the surface tension of the ink, e.g., incorporating a
15 surfactant therein. Such inks will effectively wet out on such writing surfaces and yet be erased easily even after a long dwell time on the surface.

When using conventional dry erase markers it is typically desirable for writing surface 16 to have a surface energy of greater than or equal to about 26 mJ/m². This surface energy of the writing surface prevents ink from typical dry erase and permanent
20 markers from beading up on the writing surface. Written indicia is received as a continuous layer, preventing beading up or "gaps" in the lines forming written indicia. Typical dry erase marker solvents include ethanol, isopropanol, methyl isobutyl ketone, and n-butyl acetate. In order for the marker to effectively wet out the dry erase surface without beading up, the surface energy of the dry erase surface must be greater than the
25 surface tension of the solvents in the marker ink. The solvent in the list above with the highest surface tension is n-butyl acetate, with a surface tension of about 25 mJ/m². Therefore, in one embodiment, the writing surface of the dry erase article has a surface energy greater than or equal to about 26 mJ/m². In an alternate embodiment, the writing surface of the dry erase article has a surface energy greater than or equal to about 30
30 mJ/m² as measured by as measured by ASTM D 2578-08. Additionally, written indicia can preferably be quickly removed from dry erase article with a minimum of wiping and a minimum of absorbance of ink by dry erase article. Acceptable removability of the ink is

achieved if the surface energy of the writing surface is sufficiently low to prevent the binders and other solids in the marker inks from adhering tenaciously to the writing surface. Therefore, in one embodiment, the writing surface of the dry erase article has a surface energy less than or equal to about 38 mJ/m². In an alternate embodiment, the writing surface of the dry erase article has a surface energy less than or equal to about 35 mJ/m² as measured by ASTM D 2578-08.

In some embodiments, the writing member comprises a non-tacky crosslinked polymeric layer. This polymeric layer is made from a radiation curable coating formulation containing at least one low surface energy monomer, oligomer, or polymer chosen from the group of polymerizable fluorocarbon, silicone, or hydrocarbon monomers. When radiation cured, the non-tacky crosslinked polymeric layer provides a receptive surface for inks, while simultaneously providing improved erasability and resistance to ghosting.

The non-tacky crosslinked polymeric layer may be formed by polymerizing a precursor composition, although other methods (e.g., crosslinking of a polymer or blend thereof using chemical means or ionizing radiation) may also be used. Useful precursor compositions typically comprise one or more polymerizable materials (e.g., monomers and/or oligomers, which may be monofunctional and/or polyfunctional), a curative, and optionally inorganic particles. Polymerizable materials may be, for example, free-radically polymerizable, cationically polymerizable, and/or condensation polymerizable. Useful polymerizable materials include, for example, acrylates and methacrylates, epoxies, polyisocyanates, and trialkoxysilane terminated oligomers and polymers. Preferably, the polymerizable material comprises a free-radically polymerizable material.

Useful free-radically polymerizable materials include, for example, free-radically polymerizable monomers and/or oligomers, either or both of which may be monofunctional or multifunctional. Exemplary free-radically polymerizable monomers include styrene and substituted styrenes (e.g., α -methylstyrene); vinyl esters (e.g., vinyl acetate); vinyl ethers (e.g., butyl vinyl ether); N-vinyl compounds (e.g., N-vinyl-2-pyrrolidone, N-vinylcaprolactam); acrylamide and substituted acrylamides (e.g., N,N-dialkylacrylamides); and acrylates and/or methacrylates (i.e., collectively referred to herein as (meth)acrylates) (e.g., isooctyl (meth)acrylate, nonylphenol ethoxylate

(meth)acrylate, isononyl (meth)acrylate, diethylene glycol (meth)acrylate, isobornyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, butanediol mono(meth)acrylate, β -carboxyethyl (meth)acrylate, isobutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, (meth)acrylonitrile, isodecyl (meth)acrylate, dodecyl (meth)acrylate, n-butyl (meth)acrylate, methyl (meth)acrylate, hexyl (meth)acrylate, (meth)acrylic acid, stearyl (meth)acrylate, hydroxy functional polycaprolactone ester (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxymethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxyisopropyl (meth)acrylate, hydroxybutyl (meth)acrylate, hydroxyisobutyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, ethylene glycol di(meth)acrylate, hexanediol di(meth)acrylate, triethylene glycol di(meth)acrylate, 1,3-propylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, 1,4-cyclohexanediol di(meth)acrylate, 1,5-pentanediol di(meth)acrylate, ethoxylated trimethylolpropane tri(meth)acrylate, glycerol tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, and neopentyl glycol di(meth)acrylate).

Exemplary free-radically polymerizable oligomers include those marketed by UCB Chemicals, Smyrna, Georgia (e.g., under the trade designation "EBECRYL"), and those marketed by Sartomer Company, Exton, Pennsylvania (e.g., under the trade designations "KAYARAD" or "CN").

Depending on the choice of polymerizable material, the precursor composition may, optionally, contain one or more curatives that assist in polymerizing the polymerizable material. The choice of curative for specific polymerizable materials depends on the chemical nature of the copolymerizable material. For example, in the case of epoxy resins, one would typically select a curative known for use with epoxy resins (e.g., dicyandiamide, onium salt, or polymercaptan). In the case of free-radically polymerizable resins, free radical thermal initiators and/or photoinitiators are useful curatives.

Typically, the optional curative(s) is used in an amount effective to facilitate polymerization of the monomers and the amount will vary depending upon, for example, the type of curative, the molecular weight of the curative, and the polymerization process. The optional curative(s) is typically included in the precursor composition in an amount in

a range of from about 0.01 percent by weight to about 10 percent by weight, based on the total weight of the precursor composition, although higher and lower amounts may also be used. The precursor composition may be cured, for example, by exposure to a thermal source (e.g., heat, infrared radiation), electromagnetic radiation (e.g., ultraviolet and/or visible radiation), and/or particulate radiation (e.g., electron beam or gamma radiation).

The coating composition from which the writing surface is formed should be fully cured in order to keep the marker on the surface where it can be readily removed by direct contact with a dry eraser. In particular, at least that portion of the composition that forms the writing surface should be fully cured. A variety of curing strategies are well known to those skilled in the art and suitable one(s) can be readily selected, determined in part upon the characteristics of the curable coating composition, other components of the article, as well as manufacturing facilities. Illustrative techniques for maximizing the cure of a UV cured coating composition include curing under nitrogen, using new UV bulbs, cleaning the UV bulbs before use, matching the output spectrum of the UV bulb to the absorption of the initiator, and treatment at a slow speed and/or for a longer time. In some embodiments, a certain amount of post-exposure cure may take place over time as the dry erase article ages at room temperature.

The degree of cure of a coated dry erase article may be tested by running the dry erase test described in the test method section on the sample with a one day dwell time of the writing before erasing. If the dry erase article erases better after a post-cure, then the initial cure may not be adequate. Thus a second cure treatment may be required in addition to the first cure described above. The second cure may use the same radiation source as the first cure or it may use a different radiation source. Preferred second cure methods include heat, electron beam, and gamma ray treatment.

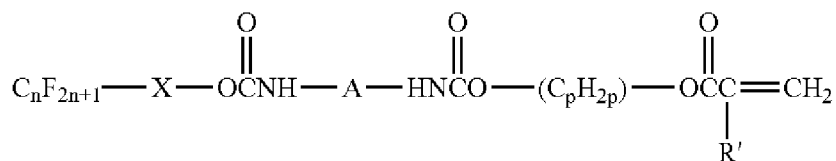
If the optional curative is a free-radical initiator, the amount of curative is preferably in a range of from about 1 percent by weight to about 5 percent by weight, based on the total weight of the precursor composition, although higher and lower amounts may also be used. Useful free-radical photoinitiators include, for example, benzoin ethers such as benzoin methyl ether and benzoin isopropyl ether, substituted benzoin ethers (e.g., anisoin methyl ether), substituted acetophenones (e.g., 2,2-dimethoxy-2-phenylacetophenone), substituted alpha-ketols (e.g.,

2-methyl-2-hydroxypropiophenone), benzophenone derivatives (e.g., benzophenone), and acylphosphine oxides. Exemplary commercially available photoinitiators include photoinitiators under the trade designation "IRGACURE" (e.g., IRGACURE™ 651, IRGACURE™ 184, and IRGACURE™ 819) or "DAROCUR" (e.g., DAROCUR™ 1173, 5 DAROCUR™ 4265) from Ciba Specialty Chemicals, Tarrytown, New York, and under the trade designation "LUCIRIN" (e.g., "LUCIRIN TPO") from BASF, Parsippany, New Jersey.

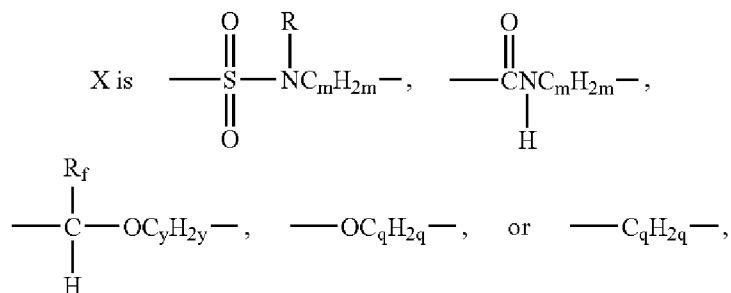
Exemplary free-radical thermal initiators include peroxides such as benzoyl peroxide, dibenzoyl peroxide, dilauryl peroxide, cyclohexane peroxide, methyl ethyl 10 ketone peroxide, hydroperoxides, for example, tert-butyl hydroperoxide and cumene hydroperoxide, dicyclohexyl peroxydicarbonate, t-butyl perbenzoate, and azo compounds, for example, 2, 2,-azo-bis(isobutyronitrile).

The low surface energy monomers, oligomers, or polymers may be chosen from the group of fluorocarbon, silicone, or hydrocarbon monomers. Fluorocarbon monomers 15 suitable for the invention include but are not limited to perfluoro acrylates or methacrylates, e.g., C₄F₉ based sulfonamide acrylates and C₃F₇ based sulfonamide acrylates. Illustrative examples of fluorocarbon monomers useful herein include C₄F₉SO₂N(CH₃)C₂H₄O-CONHC₆H₅-CH₂C₆H₅NHCO-OC₂H₄OCOCH=CH₂ also known as MeFBSE-MDI-HEA, 20 C₄F₉SO₂N(CH₃)C₂H₄O-CONH(CH₂)₆NHCO-OC₂H₄OCOCMe=CH₂, C₄F₉SO₂N(CH₃)C₂H₄O-CONH(CH₂)₆NHCO-OC₁₂H₂₄OCOCH=CH₂, and CF₃CH₂O-CONH C₆H₅CH₂C₆H₅NHCO-OC₂H₄OCOCH=CH₂. Perfluoroacrylates suitable for the invention include C₁ to C₆ perfluoroalkyl acrylates or the type RSO₂NMeC₂H₄OC(O)CH=CH₂, where R is C_nF_{2n+1} and n is an integer from 1 to 6.

25 Another family of suitable fluorochemical monomers are described in US Patent Nos. 7,279,210 (Hulteen et al.) and 7,199,197 (Caldwell et al.). These fluoroacrylate monomers are represented by the formula:



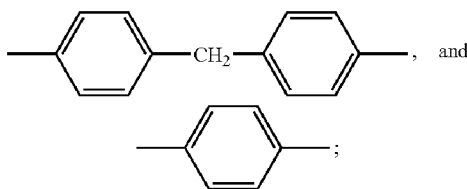
wherein n is an integer in a range of from 1 to 6, inclusive, p is an integer in a range of from 2 to 30, inclusive; and R' is H, CH₃, or F, A is a hydrocarbylene group, and



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wherein R is H or an alkyl group having 1 to 4 carbon atoms; m is an integer in a range of from 2 to 8, inclusive; R_f is C_nF_{2n+1}; y is an integer in a range of from 0 to 6, inclusive; q is an integer in a range of from 1 to 8, inclusive.

In some embodiments, A is selected from the group consisting of $-\text{C}_6\text{H}_{12}-$,



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Other fluorochemical additives suitable for the invention include perfluoropolyether urethane acrylates described in US Patent No. 7,173,778 (Jing et al.).

Fluorochemical oligomers suitable for use in dry erase articles of the invention include the commercially available chemicals FLUORAD™ FC-4430 and FC-4432 from

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3M Company, St. Paul, MN. Fluorochemical polymers suitable for use in dry erase articles of the invention include perfluoropolyether polymers with poly(alkylene oxide) repeat units, e.g., as described in PCT Application No. WO2009/076389 (Yang et al.).

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Silicone monomers suitable for the invention include but are not limited to silicone acrylate monomers. Exemplary silicone acrylate monomers suitable for use herein include BYK-371 Reactive Silicone Surface Additive, BYK-373 Reactive Silicone Surface Additive, BYK-377 Reactive Silicone Surface Additive, BYK-UV 3500 Surface Additives for Radiation Curable Systems, BYK-UV 3530 Surface Additives for Radiation Curable Systems, BYK-UV 3570 Surface Additives for Radiation Curable Systems, and BYK-SILCLEAN™ 3710 Surface Additives to Improve Surface Cleanability from BYK-

25

Chemie GmbH, Wesel, Germany. Other suitable silicone monomers include TEGORAD™ 2100, TEGORAD™ 2200N, TEGORAD™ 2250, and TEGORAD™ 2300 silicone acrylate monomers from Evonik Goldschmidt Corporation, Hopewell, VA.

Hydrocarbon monomers can be used to reduce the surface energy of a coating. Those hydrocarbon monomers are characterized by a long side chain that can form a crystalline structure on a surface. Suitable hydrocarbon monomers include but are not limited to octadecyl acrylate.

In one embodiment of the invention, low surface energy monomers, oligomers, or polymers are added to a coating formulation in a concentration sufficient to produce a cured coating with a wetting tension of from about 26 to about 36 mJ/m². Preferably, the wetting tension of the cured coating is from about 30 to about 36 mJ/m².

In some embodiments, the radiation curable material includes the foregoing oligomer(s), monomer(s) and/or polymer(s) in one or more solvents along with a volume of optional particles or nanoparticles, e.g., to impart increased hardness and durability to the writing member.

Nanoparticles can be surface modified which refers to the fact that the nanoparticles have a modified surface so that the nanoparticles provide a stable dispersion. "Stable dispersion" refers to a dispersion in which the colloidal nanoparticles do not agglomerate after standing for a period of time, such as about 24 hours, under ambient conditions, e.g., room temperature (i.e., about 20 to about 22°C), and atmospheric pressure, without extreme electromagnetic forces.

Surface-modified colloidal nanoparticles can optionally be present in a polymer coating used as a coatable composition herein with nanoparticles present in an amount effective to enhance the durability of the finished or optical element. The surface-modified colloidal nanoparticles described herein can have a variety of desirable attributes, including, for example, nanoparticle compatibility with a coatable composition such that the nanoparticles form stable dispersions within the coatable composition, reactivity of the nanoparticle with the coatable composition making the composite more durable, and a low impact or uncured composition viscosity. A combination of surface modifications can be used to manipulate the uncured and cured properties of the composition. Surface-modified nanoparticles can improve optical and physical properties of the coatable composition such as, for example, improved resin mechanical strength, minimized viscosity changes

while increasing solids volume loading in the coatable composition and maintain optical clarity while increasing solid volume loading in the coatable composition.

In some embodiments, the nanoparticles are surface-modified nanoparticles. Suitable surface-modified colloidal nanoparticles can comprise oxide particles.

5 Nanoparticles may comprise a range of particle sizes over a known particle size distribution for a given material. In some embodiments, the average particle size may be within a range from about 1 nm to about 100 nm. Particle sizes and particle size distributions may be determined in a known manner including, for example, by transmission electron microscopy (“TEM”). Suitable nanoparticles can comprise any of a
10 variety of materials such as metal oxides selected from alumina, tin oxide, antimony oxide, silica, zirconia, titania and combinations of two or more of the foregoing. Surface-modified colloidal nanoparticles can be substantially fully condensed.

In some embodiments, silica nanoparticles can have a particle size ranging from about 5 to about 100 nm. In some embodiments, silica nanoparticles can have a particle
15 size ranging from about 10 to about 30 nm. Silica nanoparticles can be present in the coatable composition in an amount from about 10 to about 100 phr. In some embodiments, silica nanoparticles can be present in the coatable composition in an amount from about 30 to about 90 phr. Silica nanoparticles suitable for use in the coatable compositions of the present invention are commercially available from Nalco Chemical Co. (Naperville, IL)
20 under the product designation NALCO™ COLLOIDAL SILICAS. Suitable silica products include NALCO products 1040, 1042, 1050, 1060, 2327 and 2329. Suitable fumed silica products include, for example, products sold under the AEROSIL™ series OX-50, -130, -150, and -200 available from DeGussa AG, (Hanau, Germany), and CAB-O-SPERSE™ 2095, CAB-O-SPERSE™ A105, and CAB-O-SIL™ MS available from
25 Cabot Corp. (Tuscola, IL). Surface-treating the nanosized particles can provide a stable dispersion in the coatable composition (e.g., a polymeric resin). Preferably, the surface-treatment stabilizes the nanoparticles so that the particles will be well dispersed in the coatable composition and results in a substantially homogeneous composition. Furthermore, the nanoparticles can be modified over at least a portion of its surface with a
30 surface treatment agent so that the stabilized particle can copolymerize or react with the coatable composition during curing.

Silica nanoparticles can be treated with a surface treatment agent. Surface treatment agents suitable for particles to be included in the coatable composition include compounds such as, for example, isooctyl trimethoxy-silane, N-(3-triethoxysilylpropyl) methoxyethoxyethoxy ethyl carbamate (PEG3TES), SILQUEST™ A1230, N-(3-
5 triethoxysilylpropyl) methoxy ethoxyethoxyethyl carbamate (PEG2TES), 3-(methacryloyloxy)propyl trimethoxysilane, 3-acryloyloxypropyltrimethoxysilane, 3-(methacryloyloxy)propyltriethoxysilane, 3-(methacryloyloxy)propylmethyldimethoxysilane, 3-(acryloyloxypropyl) methyldimethoxy silane, 3-(methacryloyloxy)propyldimethylethoxysilane, 3-
10 (methacryloyloxy)propyldimethyl ethoxysilane, vinyl dimethylethoxysilane, phenyltrimethoxysilane, n-octyltrimethoxysilane, dodecyltrimethoxysilane, octadecyltrimethoxysilane, propyltrimethoxysilane, hexyltrimethoxy silane, vinylmethyldiacetoxysilane, vinylmethyldiethoxysilane, vinyltriacetoxysilane, vinyltriethoxysilane, vinyltriisopropoxysilane,
15 vinyltrimethoxysilane, vinyltriphenoxysilane, vinyltri-t-butoxysilane, vinyltris-isobutoxysilane, vinyltriisopropenoxysilane, vinyltris(2-methoxyethoxy)silane, styrylethyltrimethoxysilane, mercaptopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, acrylic acid, methacrylic acid, oleic acid, stearic acid, dodecanoic acid, 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (MEEAA), beta-
20 carboxyethylacrylate, 2-(2-methoxyethoxy)acetic acid, methoxyphenyl acetic acid, and mixtures of two or more of the foregoing.

In some embodiments, the average particle sizes (e.g., particle diameter) may be within the range from about 1 nm to about 1000 nm. In addition to the foregoing particle sizes, use of smaller and larger average particle sizes are also contemplated. In
25 embodiments of the invention, at least a portion of the foregoing particles may be surface modified in the manner described above. In other embodiments, all of the particles are surface modified. In still other embodiments, none of the particles are surface modified.

As will be understood, coating compositions used to make writing members of the invention may include optional additives to enhance or control characteristics as desired,
30 e.g., rheology modifiers such as JAYLINK™ Rheology Modifiers, colorants (e.g., dyes and/or pigments), fire retardants, antioxidants, stabilizers, antiozonants, plasticizers, UV absorbers, hindered amine light stabilizers (HALS), etc.

Backing Member

In some embodiments, e.g., where the writing member is not sufficiently self supporting or where other properties are desired of the dry erase article, e.g., imparted
5 with magnetic properties, curl resistance properties, tear resistance properties, dimensional stability, color, etc., the dry erase article will further comprise a backing member on the rear surface of the writing member. Depending upon the embodiment, the backing member may be single or multilayer.

10 Illustrative examples of suitable substrates for use as a backing member include but are not limited to glass, , paper, coated paper, paper film laminates, polymeric films, polymeric sheets and metallic foils, metal sheets, porcelain sheets, etc. Polymeric films and sheets include but are not limited to polyester, polypropylene, polyethylene, polystyrene, cellulose acetates, polycarbonate, polyacrylate and polyvinyl chloride. Polymer
15 films and sheets may include copolymers, blends, or coextruded multilayer films of the aforementioned polymers or other polymers. If desired, the backing may include or even consist of an adhesive on the rear surface thereof to facilitate bonding of the resultant dry erase article to a substrate or surface.

In embodiments where the good projection performance are desired of the dry erase article, the writing member will be preferably be substantially clear and the backing
20 member will have reflective characteristics. For example, the projection member disclosed in US Patent Application No. 12/684,565, filed December 15, 2009, could be used in dry erase articles of the invention.

If desired, the backing member may be opaque and/or colored to impart desired appearance to the resultant dry erase article. Also, decorative or organizational graphics,
25 headings, etc. may be provided in the article so as to be visible to viewers, e.g., legends embedded within the writing member, on the rear surface of the writing member, on the front surface of the backing, etc. with desired decorative emblems, information headings (e.g., "NAME", "IN", "OUT", and so forth).

30 Dry Erase Markers

In some embodiments, dry erase articles of the invention may be used with a variety of conventional dry erase markers.

Commercially available dry erase marker inks typically have a surface tension of less than about 30 mJ/m². There are two common types of dry erase markers, i.e., alcohol solvent based and ketone solvent based markers. The solvents in alcohol markers are typically ethanol and isopropanol. The solvents in ketone based markers are typically methyl isobutyl ketone and n-butyl acetate. The surface tension values of these solvents is listed in the table below.

Table 1. Surface tension of marker solvents

Solvent	Surface Tension (mJ/m ²)
Ethanol	22.8
Isopropanol	23.0
methyl isobutyl ketone	23.6
n-butyl acetate.	25.1

For complete wet out of the dry erase marker, the wetting tension of the dry erase board needs to be greater than the surface tension of the marker ink. Thus the wetting tension of the surface, as measured by ASTM D2578, typically should be greater than 25 mJ/m² for commercially available markers to wet out on the surface.

In some embodiments of the invention, wherein the writing surface has a super low surface wetting tension, i.e., less than about 30 mJ/m², an effective amount of one or more surfactants can be added to the ink in dry erase markers in order to reduce the surface tension of the ink formulations. The surfactants can be anionic, cationic, or non-ionic. Because of the restricted selection of markers which can be used to write effectively on such super low wetting tension, such dry erase articles are protected from attempts to place graffiti thereon or inadvertent use of the wrong marker, such as a permanent marker instead of a dry erase marker.

Illustrative examples of suitable surfactants include but are not limited to FLUORAD™ FC-170C, FC-430, and FC-171 from 3M Company, St. Paul, MN, SIVENTO DYNASYLAN™ F8810 from Evonik Industries, Parsippany, NJ, FOMBLIN™ C from Ausimont Inc., Thorofare, NJ, Silane B-1092 from Gelest Inc., Kent, ME, FLUOROLINK™ 3, from Solvay Solexis, West Deptford, NJ, and DYNASYLAN™ FC-8261 from Huls America, Cincinnati, OH. The aforementioned FLUORAD™ FC-4430 and FC-4432 may be used as surfactants in some ink formulations in accordance with the invention.

Examples

The invention will be further explained with the following illustrative, non-limiting examples.

5 Test Methods

The following test methods were used.

Marker Dewetting: Dry erase surfaces were marked with 14 different markers comprising 7 brands of dry erase markers. The dry erase markers were AVERY™
10 MARKS-A-LOT™ (Avery-Dennison, Pasadena, Cal.), BEIFA™ private label markers (Beifa, Tokyo, Japan), BIC™ Dry Erase markers (BIC Corporation, Milford, Conn.), DIXON™ Dry Erase Markers (Dixon Ticonderoga Co., Heathrow, Fla.), EXPO™ Bold (Sanford Corp., Bellwood, IL), EXPO™ Low Odor (Sanford Corp.), and QUARTET™
15 Markers (Acco, Inc, Lincolnshire, IL). All of the markers had a chisel point. Two colors of marker from each brand were chosen, one black and the other red, green, or blue. A typical dry erase sample was about the size of a sheet of paper. For each marker brand, a horizontal space about 2.5 cm high on the sample was reserved for that marker brand. The first marker was used to write the marker brand name on the left hand side of the 2.5 cm
20 high space and the second marker was used to write the same marker brand name on the right hand side of the 2.5 cm high space. In this manner, all the writing from each marker brand is lined up in one erasable horizontal line.

After marking on the inventive dry erase surface, each ink line was examined for dewetting. Dewetting or beading up of the dry erase ink was evidenced by the appearance of gaps in the ink line or a shrinking of the ink line. The total number of markers that
25 dewet was calculated. Fourteen different markers were utilized in the writing test, therefore the range of possible dewetting scores is 0 to 14. For example, if no markers dewet, the dewetting score was zero. If 10 markers dewet, the score was 10.

Dry Erase Writing Removal: After writing on the subject writing surface and
30 aging of the writing at room temperature as indicated, removability of dry erase writing was tested as follows. The sample was placed on a hard, flat surface. An EXPO™ Dry Eraser (Sanford Corp.) was used to erase the writing. The area of the eraser in contact

with the writing surface was about 12.5 cm x 5 cm. A 12.5 cm x 5 cm brass weight weighing 2.5 kg was placed on top of the eraser, resulting in a pressure of 0.4 N/cm². This weighted eraser was passed over the first line of marker writing without additional hand pressure. The first line of writing included the writing from the two markers of the first brand. The number of passes of the eraser required to remove all but a few specs of marker writing were counted. If the writing was still readable after 10 strokes with the eraser, the erasing was halted. Erasing was then continued with a wet paper towel up to 10 strokes. The total number of strokes per marker brand are recorded and summed over the seven brands. In some cases a single stroke of the eraser removed all the writing from both markers. In other cases it took more than one stroke to remove the writing. The minimum dry erase removal score is 7 because there are a total of 7 lines of dry erase marker writing.

Wetting Tension: Wetting tension of the inventive dry erase surfaces was measured according to ASTM D 2578-08, 01 September 2009. All surfaces were first cleaned with isopropanol and a paper towel. The surface was allowed to dry for 10 minutes. Wetting tension pens were obtained from UV Process Control, Chicago, IL, covering the range of 30 to 48 mJ/m² in steps of 2 mJ/m². The pure solvents listed in Table 2 were utilized to measure the wetting tension of surfaces below 30 mN/m².

20

Table 2. Surface Tension of Pure Liquids

Solvent	Surface Tension (mJ/m ²)
n-Heptane	20.3
Isopropanol	23.0
n-Decane	23.8
Ethyl butyrate	25.8
n-Hexadecane	27.5
Toluene	28.4
Ethyl cellosolve	30.0

The liquid was applied to the dry surface by the pen or a cotton tipped applicator. If the liquid did not completely bead up or if the liquid maintained a continuous film without gaps for 2 seconds, the liquid wets the surface. The wetting tension of the film is the highest surface tension pen or liquid that wets out the film for 2 seconds.

25

Adhesion to the dry erase surface: Relative peel adhesion of a standard tape to a writing surface is a measure of the relative surface energy of the surface. The peel adhesion of 3M™ SCOTCH™ 810 Magic Tape to writing surfaces was measured. The surface was first cleaned with isopropanol and dried overnight at 23°C (73°F) and 50% RH. A ball slide was inserted into the lower jaw of a tensile tester (MTS, Eden Prairie, MN). 3M™ High/Low Tack 9415 Double Coated Tape was applied to the ball slide with the repositionable adhesive facing up. The dry erase surface was then applied to the 9415 tape. A length of 2.54 cm wide 810 tape was adhered to the dry erase surface with at least 20 cm of tape hanging over the front edge of the surface. The tape was rolled onto the film with a standard 2 kg rubber covered roller in four individual passes at a speed of about 64 cm/min. The free end of the tape was attached to the upper jaw of the tensile tester. The tape was peeled off the film at 90° at a rate of 30 cm/min maintaining the 90° peel by moving the ball slide at the same rate, 30 cm/min. The average peel adhesive value was recorded.

15

Materials

Materials utilized in the examples and comparatives are shown in Table 3.

Table 3. Materials

Material	Description	Source
FC-4432	3M NOVEC™ Fluorurosurfactant	3M Company St. Paul, MN
906 hardcoat	UV curable acrylic hardcoat, described in US Patent No. 5,677,050, Example 1	3M Company
HFPO-UA	Hexafluoropropylene oxide urethane acrylate	3M Company
HFPO-PEG	Hexafluoropropylene oxide polyethylene glycol urethane acrylate	3M Company
MeFBSEA	$C_4F_9SO_2NMeC_2H_4OC(O)CH=CH_2$	3M Company
White PET	3 mil (76 micron) thick white polyester film, W54B, two side primed	Mitsubishi PET Film LLC Greer, SC
Clear PET	2 mil (50 micron) thick clear polyester film, one side primed. Coating was applied to the primed side of the film.	3M Company
IRGACURE™ 184	UV initiator	Ciba Specialty Chemicals Newport, DE
SR 444	Multifunctional acrylate monomer	Sartomer Company Exton, PA
SR 344	Multifunctional acrylate monomer	Sartomer Company
SR 351LV	Multifunctional acrylate monomer	Sartomer Company
IPA	Isopropanol, reagent grade.	Mallinckrodt Baker Phillipsburg, NJ
Ethyl acetate	Ethyl acetate, 99% urethane grade	Brenntag Great Lakes Butler, WI
MEK	Methyl ethyl ketone, reagent grade	Mallinckrodt Baker
n-Heptane	Reagent grade	Mallinckrodt Baker
n-Decane	99+%	Alpha Aesar Ward Hill, MA
n-Hexadecane	99+%	Alpha Aesar
Ethyl butyrate	Reagent grade	MP Biomedicals, Inc. Solon, OH
Toluene	Reagent grade	EMD Chemicals Gibbstown, NJ
Ethyl cellosolve	99%	Sigma Aldrich St. Louis, MO
#810, #9415	Adhesive tapes	3M Company
EXPO™ Low Odor markers	Dry erase markers	Acco, Inc. Lincolnshire, IL

Markers: For complete wet out of the dry erase marker, the wetting tension of the dry erase surface needs to be greater than the surface tension of the marker fluid.

Typically, the wetting tension of the surface needs to be greater than about 28 mJ/m² for all markers to write on the dry erase surface.

5 A solution was prepared containing 10% FC-4432 surfactant by weight in isopropanol. With a syringe, 0.5 mL of the surfactant solution was injected into the tip of black and green EXPO™ Low Odor dry erase markers and allowed to penetrate and mix overnight.

10 Preparation of Functionalized Nano-silica: A 12 liter flask was charged with 3000 g of aqueous colloidal silica solution (such as NALCO™ 2327 from Nalco Company) and stirring was started. Then 3591 g of 1-methoxy-2-propanol (such as DOWANOL™ PM from Dow Chemical, Midland, MI) was added. In a separate container, 189.1 g of 3-methacryloxy propyltrimethoxysilane (such as SILQUEST™ A-174 from Momentive

15 Performance Materials, Wilton, CT) was mixed with 455 g of 1-methoxy-2-propanol. This pre-mix solution was added to the flask, rinsing with 455 g of 1-methoxy-2-propanol. The mixture was heated to 80°C for about 16 hours. The mixture was cooled to 35°C. The mixture was set up for vacuum distillation (30 to 35 Torr (4000 to 4700 Pa), 35 to 40°C) with a collection flask. An additional 1813.5 g of 1-methoxy-2-propanol was added to the

20 reaction flask part way through the distillation. A total of 6784 g of distillate was collected. The mixture was tested for % solids by drying a small sample in a tared aluminum pan for 60 minutes in a 105°C oven. The mixture was found to be 52.8% solids. An additional 250 g of 1-methoxy-2-propanol was added and the mixture was stirred. The % solids was tested and found to be 48.2%. The mixture was collected by filtering

25 through cheesecloth to remove particulate debris.

Example 1 – 906 hardcoat with 0.075% HFPO-UA: The synthesis of HFPO-UA is described in US Patent No. 7,173,778. The HFPO-UA was diluted to 25% solids in MEK. To a solution of 906 hardcoat was added a solution of HFPO-UA in MEK to yield a final

30 concentration of 0.075% HFPO-UA solids to 906 hardcoat solids. The solution was then diluted to 25% solids with ethyl acetate. This formulation was coated on a 9 in (23 cm) wide continuous coater that included stations for coating, drying, UV curing, and roll up of

the coated film. The coating formulation was applied by a coating die onto 3 mil (76 micron) thick white polyester film. After coating, the film was passed through a 30 ft (9.1 m) long forced air oven and dried at 130°F (54°C). Then the film went through a nitrogen purged UV cure chamber containing an H⁺ bulb. The oxygen concentration in the cure chamber was less than 100 ppm. The line speed on the coater was 50 feet/min (15.2 m/min) and the dry thickness of the coating on the film was 2 μm.

Example 2 – 906 hardcoat with 10% MeFBSEA,

(C₄F₉SO₂NMeC₂H₄OC(O)CH=CH₂):

MeFBSEA was synthesized by the procedure described in PCT Application No. WO200130873 (Savu et al.). MeFBSEA was added to the 906 hardcoat at a value of 10% to solids. After mixing, the solution was diluted to 30% solids with MEK. The solution was coated on 2 mil (50 micron) clear polyester film with a #6 Mayer rod. The coated film was dried at 100°C for one minute. The film with the dry coating was passed through a nitrogen purged UV curing chamber containing an H bulb.

Example 3 – 906 hardcoat with 15% MeFBSEA,

(C₄F₉SO₂NMeC₂H₄OC(O)CH=CH₂): MeFBSEA was synthesized by the procedure described in PCT Application No. WO200130873. MeFBSEA was added to the 906 hardcoat at a value of 15% to solids. After mixing, the solution was diluted to 30% solids with MEK. The solution was coated on 2 mil clear polyester film with a #6 Meier rod. The coated film was dried at 100°C for one minute. The film with the dry coating was passed through a nitrogen purged UV curing chamber containing an H bulb.

Example 4 – Hardcoat 2 with 0.075% HFPO-UA: Hardcoat 2 was made at 30%

solids according to the formulation in Table 4. The preparation of the functionalized nano-silica is described in the Examples section. Some HFPO-UA at 25% solids in MEK was added to the solution to make 0.075% HFPO-UA to solids. Then the formulation was diluted to 25% solids with ethyl acetate. This formulation was coated, dried, and cured by the same method as in Example 1.

Table 4. Formulation of Hardcoat 2

Material	Formulation (wt. %)	Percent of Solids
Nano-silica functionalized	19.9%	35.9%
IRGACURE™ 184	0.6%	2.5%
SR 444	13.3%	53.2%
SR 344	2.1%	8.3%
Isopropanol	24.6%	0.0%
Ethyl Acetate	39.4%	0.0%

Example 5 – Hardcoat 2 with 0.075% HFPO-PEG: Preparation of the HFPO-PEG monomer is described in PCT Application No. WO 2009/076389. Hardcoat 2 was made at 30% solids according to the formulation in Table 4. Some HFPO-PEG at 25% solids in MEK was added to the hardcoat 2 solution to make 0.075% HFPO-PEG to solids. Then the formulation was diluted to 25% solids with ethyl acetate. This formulation was coated, dried, and cured by the method described in Example 1.

Example 6 – Hardcoat 2 with 1.4% HFPO-UA: Hardcoat 2 was made at 30% solids according to the formulation in Table 4. Some HFPO-UA at 25% solids in MEK was added to the solution to make 1.4% HFPO-UA to solids. Then the formulation was diluted to 25% solids with ethyl acetate. This formulation was coated, dried, and cured by the same method as in Example 1.

Example 7: A film was made with 906 hardcoat containing 0.15% HFPO-UA to solids. A solution of HFPO-UA in MEK was added to 3M 906 hardcoat to give a concentration of 0.075% HFPO-UA solids to 906 hardcoat solids. The hardcoat was diluted to 25% solids with ethyl acetate. This formulation was coated on the pilot coater onto 3 mil thick white PET film as described in Example 1.

Example 8: Hardcoat 2 was made at 30% solids according to the method in Example 4. Some FC-4430 at 25% solids in MEK was added to the solution to make 1.5% FC-4430 to solids ratio in the formulation. The formulation was then diluted to 25% solids with ethyl acetate. This formulation was coated, dried, and cured by the same method as in Example 1. The dry coating thickness was 2.0 μm .

Example 9: Hardcoat 2 was made at 30% solids according to the method in example 4. Some FC-4430 at 25% solids in MEK was added to the solution to make 2.5% FC-4430 to solids ratio in the formulation. The formulation was then diluted to 25% solids with ethyl acetate. This formulation was coated, dried, and cured by the same method as in Example 1. The dry coating thickness was 2.0 μm .

Example 10 – Hardcoat 3 with 1% MeFBSEA: This hardcoat was made at 30% solids according to the formulation in Table 4. The preparation of the functionalized nano-silica is described in the Examples section. Solid MeFBSEA was dissolved in ethyl acetate to make a 25% solids solution. The five materials listed in Table 5 were added to a large stainless steel beaker and mixed. The formulation was diluted to 25% solids with ethyl acetate in the same beaker. This formulation was coated, dried, and cured by the same method as in Example 1. After coating, the film was heated for two days at 50°C.

Table 5. Formulation of Hardcoat 3

Material	Formulation (wt. %)	Percent of Solids
Nano-silica functionalized	26.7%	40.0%
IRGACURE™ 184	0.73%	2.4%
SR 351LV	17.0%	56.6%
MeFBSEA	0.30%	1.0%
Ethyl Acetate	55.3%	0.0%

Comparative Example C1 – 906 hardcoat: The 906 hardcoat was diluted to 25% solids with ethyl acetate. This formulation was coated on the pilot coater onto 3 mil thick white PET film. This formulation was coated, dried, and cured by the same method as in Example 1. The dry coating thickness of the hardcoat was 2 μm .

Comparative Example C2 – Hardcoat 2: The hardcoat 2 formulation of Example 4 was prepared at 25% solids. This formulation was coated, dried, and cured by the same method as in Example 1. The dry coating thickness of the hardcoat was 2 μm .

Comparative Example C3 – QUARTET™ Total Erase Board: This board, from Acco Corp. consists of a multifunctional acrylate coating on top of coated paper on top of a medium density fiberboard panel.

5 Comparative Example C4: JFE porcelain steel sheet, available from JFE Metal products and Engineering Inc., Tokyo, Japan.

Comparative Example C5: POLYVISION™ porcelain steel dry erase sheet from Polyvision Corp., Suwanee, GA.

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Results

The wetting tension, dewetting, and tape adhesion of dry erase writing surfaces are shown in Table 6.

Table 6. Wetting Tension, Dewetting, and Tape Adhesion

Example	Wetting Tension (mJ/m ²)	Number of markers dewetting	Adhesion of 810 tape (g/25mm)
1	27.5	0	286
2	32	0	323
3	30	0	280
4	25.8	0	309
5	27.5	0	321
6	<20.3	14	141
7	23.8	14	Not measured
8	30	0	Not measured
9	30	0	Not measured
10	34	0	Not measured
C1	36	0	383
C2	38	0	391
C3	38	0	Not measured
C4	40	0	Not measured
C5	38	0	Not measured

15

The writability results for the dry erase markers mixed with surfactant(s) are shown in Table 7.

Table 7. Wet out of EXPO™ Low Odor markers on Example Films

Marker Color	Surfactant added	Wet out on Example 1 film	Wet out on Example 7 film
Black	None	Yes	No
Black	FC-4432	Yes	Yes
Green	None	Yes	No
Green	FC-4432	Yes	Yes

5

Selected examples were tested for dry erase writing removal after a dwell time of one day and two weeks on the example surfaces (Table 8). Removal of all dry erase markers with seven passes of the dry eraser indicates easy removal of the writing. A removal score of more than seven indicates that a ghost image of the writing of one or more markers remained on the board after one pass of the eraser.

10

Table 8. Dry Erase Testing Of Selected Examples

Example	Hardcoat	Additive	Dry Erase 1 day RT	Dry Erase 2 week RT
4	906	HFPO-UA	7	7
CE1	906	None	7	9
10	3	MeFBSEA	7	7
CE3		None	7	17

Although the present invention has been fully described in connection with the preferred embodiments thereof with reference to the accompanying drawings, it is to be noted that various changes and modifications are apparent to those skilled in the art. Such changes and modifications are to be understood as included within the scope of the present invention as defined by the appended claims unless they depart therefrom.

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The complete disclosure of all patents, patent documents, and publications cited herein are incorporated by reference in their entirety. The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims.

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What is claimed is:

1. A dry erase article having a writing surface that has a surface wetting tension of less than about 38 mJ/m².
- 5 2. The article of claim 1 wherein said writing surface has a surface wetting tension of from about 26 to less than about 38 mJ/m².
- 10 3. The article of claim 1 wherein said writing surface has a surface wetting tension of from about 30 to less than about 38 mJ/m².
- 15 4. The article of claim 1 wherein said writing surface has a surface wetting tension of from about 20 to about 30 mJ/m².
- 15 5. The article of claim 1 wherein said writing surface comprises the radiation cured product of a radiation curable coating composition comprising at least one low surface energy monomer, oligomer, or polymer.
- 20 6. The article of claim 5 wherein said radiation curable coating composition comprises at least one multifunctional acrylate monomer.
- 25 7. The article of claim 5 wherein said radiation curable coating composition optionally comprises silica nano-particles or acrylate functional silica nano-particles.
- 25 8. The article of claim 5 wherein at least the portion of said radiation curable coating at the writing surface is fully cured.
- 30 9. The article of claim 5 wherein said radiation cured product is subject to an optional second cure by heat, IR radiation, UV radiation, electron beam, or gamma ray radiation.

10. The article of claim 5 wherein said low surface energy monomer, oligomer, or polymer is a fluorochemical having one or more side chains having the formula C_nF_{n-1} wherein n is an integer from 1 to 6.

5 11. The article of claim 5 wherein said low surface energy monomer, oligomer, or polymer is a silicone acrylate material.

12. The article of claim 5 wherein said low surface energy monomer, oligomer, or polymer is a long chain hydrocarbon containing at least one polymerizable acrylate group.

10

13. The article of claim 12 wherein said long chain hydrocarbon is octadecyl acrylate.

14. A method comprising:

- 15 a) providing a dry erase article of claim 1;
b) writing first written matter on said writing surface using a dry erase marker comprising an ink having surface tension that is less than the surface energy of the writing surface; and
c) erasing at least a portion of said first written matter with no more than 2 passes of a dry eraser

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15. The method of claim 14 wherein during said erasing said dry eraser is subjected to a pressure of up to about 0.4 N/cm^2 .

16. The method of claim 14 wherein said writing is done by hand.

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17. The method of claim 14 wherein said dry erase marker fluid has a surface tension of about 20 mJ/m^2 to about 30 mJ/m^2 .

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18. The method of claim 17 wherein said dry erase marker ink contains a surfactant to reduce the surface tension of said ink to less than the surface energy of said writing surface.

19. The method of claim 14 wherein said erasing step is performed at least about 6 hours after said writing step.

5 20. The method of claim 14 wherein said erasing step is performed at least about 24 hours after said writing step.

21. The method of claim 14 wherein said erasing step is performed at least about 7 days after said writing step.

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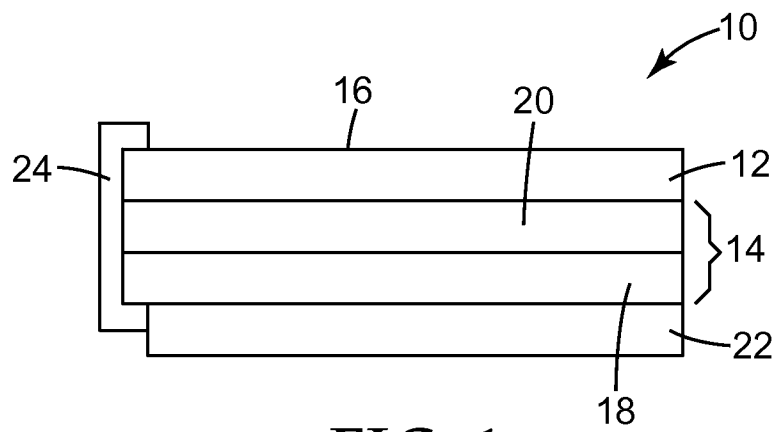


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/022618

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B43L1/00
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 B43L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/003307 A1 (HESTER JONATHAN F [US] ET AL) 5 January 2006 (2006-01-05)	1-5,9, 14-21
Y	page 1, paragraph 1 - page 7, paragraph 60 -----	6-8
X	WO 2004/020221 A1 (3M INNOVATIVE PROPERTIES CO [US]) 11 March 2004 (2004-03-11)	1-5,9
Y	page 28, line 18 - page 40, line 26 -----	6-8
X	US 3 563 782 A (LIBERMAN ISAAH U ET AL) 16 February 1971 (1971-02-16)	1-5,9
Y	the whole document -----	6-8
X	US 2006/024463 A1 (GUSTAFSON FREDERICK J [US] ET AL) 2 February 2006 (2006-02-02)	1-5,9
Y	the whole document -----	6-8

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"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.
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 28 March 2011	Date of mailing of the international search report 08/04/2011
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Kelliher, Cormac
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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