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OIL-IN-WATER TYPE EMULSION FOR FLAMEPROOFING FABRICS

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This invention relates to the treatment of fabrics to produce desirable color and flame-resistant properties therein. In particular, the invention relates to a new group of novel oil-in-water type emulsions, and to their preparation and use whereby in a single treatment color and flame-resisting materials can be readily deposited on various fabrics from an aqueous medium. The instant application constitutes a continuation-in-part of my copending application Serial No. 633,854, filed December 8, 1945, now abandoned.

Coloring of fabrics by padding and printing is one of the oldest arts. Flame-proofing of fabrics to be used for purposes of decoration and/or concealment, though a newer art, has come to be widely demanded. When both color and flame resistance are required in the same fabric, however, the processing steps required have been complicated, expensive and in many cases wholly unsatisfactory. This has been due largely to the necessity for separate and successive operations which were required because the practice of imparting these properties involved the use of incompatible materials. Even successive treatments were not wholly successful because of the adverse effect of the flame-resistant coatings on the coloration and vice versa.

Because of this situation, much work has been done in attempts to combine these operations into fewer processing steps. Here again, incompatability of the materials introduced many difficulties. On the whole, such procedures, like the earlier successive treatments, were either unsuccessful or unsatisfactory for one or more reasons such as: expense; alteration of the hand; limited color range; requirement of excessive amounts of volatile, organic solvents or a substantially all solvent system; physical difficulty or fire hazard in application; requirement of special drying techniques; lack of light fastness; lack of crock-resistance; lack of permanence of flame-resistance; inability to stand weathering; wastefulness in use or application; and difficulty in changing the color to be applied or in cleaning the apparatus used.

There remains, then, a demand for a procedure whereby color and flame resistance can be imparted in a simple, effective, relatively-inexpensive treatment. Such a procedure and material

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for use therein should be free from the objectionable difficulties noted above and should not result in the production of articles which are subject to such troubles.

It is, therefore, the principal object of the present invention to produce a novel composition adapted to deposit the desired coloring and flame-proofing materials on the fabric in a single treatment and from an aqueous medium. It is also an object of the invention to devise a treating process which is adapted to handle a wide range of color without being subject to color distortion by the flame proofing. It is a still further object to produce articles which have a soft, flexible hand and are capable of withstanding extended weathering without excessive loss of either color or flame-resistance.

In accordance with the present invention these and other objects are accomplished by the manufacture and use of novel oil-in-water emulsions. Successful use of such materials to solve the problem completely is quite remarkable in view of the diversity of materials used, the lack of water-solubility of the majority of them and the fact that similar attempts using common solvents lead to many complications.

While the present invention is not primarily intended to be limited to particular materials, certain basic ingredients are commonly found therein. These ingredients may be roughly grouped into four types. First, there is the question of the external medium, which in the present invention is aqueous and preferably thickened. Second, is a group of flame-proofing ingredients which include suitably proportioned quantities of a properly halogenated organic material and a fire-resistant, uncolored pigment potentially reactive therewith. Third, is the coloring material which in the present invention is a pigment or a group of pigments. Finally, because colored pigments have no affinity for the fabric, a binder must be provided therefor. These are basic constituents which are present whether or not additional components are used. In the following discussion of the use of these ingredients, the proportions given are for the amount which will be present in the emulsion as applied to the fabric.

As has been noted, for the continuous phase an aqueous medium is used, and preferably one which is suitably thickened. For this thickening

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a water-soluble material should be used which itself is colorless but which may be deposited on the fabric to be treated. In accordance with the present invention, the use of a lower alkyl cellulose derivative such as methyl cellulose or "Methocel" has proved wholly satisfactory. In using methyl cellulose it has been found, for example, that about a 0.5% solution of a 3000–4000 centipoise grade is very effective for most purposes. However, if so desired, other commercially available hydrophilic colloids such as for example sodium alginate, ammonium caseinate, a carboxymethyl-cellulose and the like or various gums such as tragacanth, karaya, locust bean and the like may be used. When other thickeners are used the amount should be such as to produce an approximately similar viscosity. Because of the difference in weights of these materials as well as their differing effect on viscosity when in solution, the amount of hydrophilic colloid used will vary, usually between about 0.1 and 10% by weight, based on the water.

Because the principal composition is an oil-in-water type emulsion it is often desirable although not always necessary, that the continuous phase contain dispersing and/or emulsifying agents to maintain the necessary interfaces between the phases. Preferably these take the form of water-soluble soaps, for example, ammonium oleate, ammonium stearate and the like. For most purposes the ammonium soaps are preferable to those of sodium or potassium. About 0.25–4.0% by weight of the emulsion of ammonium oleate, or a corresponding amount of a chemical equivalent may be used. As will be brought out in the examples below, about 1.0–1.5% is a good average practice. Instead of fatty-acid soaps, other materials such for example as ammonium caseinate; sulfonated oils such as sulfonated castor oil, mahogany soap and the like; and sulfated materials such as the sodium salt of the sulfated higher aliphatic alcohols may be used. When such emulsifying agents are present, it is desirable that the external medium be alkaline. This is readily accomplished by adding aqueous ammonia or an organic base such as morpholine or the like. For this reason, a good practice is to add more ammonia, or its equivalent, than is required to saponify the fatty-acids which are added to provide the desired amount of soap. As is shown in the following examples, a good average practice is to use about 1.2–1.7% by weight as 28% aqueous NH_4OH, or its equivalent. If a preformed soap is added, the amount of ammonia, or its equivalent base, is adjusted therefor, providing only the amount requisite to control the pH.

These dispersing and/or emulsifying agents may be added per se to the continuous phase. If so, they may be conveniently added along with the hydrophilic colloid. On the other hand, it may be desirable to form these constituents in situ. In the later case it is usually desirable to add only the alkaline component to the water phase and to add the acidic component with the dispersed phase. In this way the two components can react and form the desired agent during the incorporation of the dispersed phase.

Having prepared the thickened aqueous material for the continuous phase, the dispersed phases containing the halogenated organic material, the flame-resistant pigment, the binder and the coloring pigments are prepared. These are then added stepwise to the aqueous material and the whole blended into a smooth, stable emulsion. For best results, so far as practical application is concerned, blending should be continued until the bulk of the dispersed material is reduced to a size of approximately 30 microns or less.

With regard to the flame-proofing ingredients, the nature of the chlorinated organic hydrocarbon used may be quite widely varied. It should, however, possess certain properties. In particular, it should be substantially colorless, fire-resistant, water-insoluble, readily available or easily prepared. Preferably it should be a fluid. However, materials which are semi-fluid, that is, of waxy consistency may be used by adding thereto a sufficient amount of a suitable solvent thinner to impart the requisite fluidity. Several materials are well suited for use as flame-proofing ingredients. Chlorinated paraffin is excellent. Certain chlorinated elastomers, such as partially polymerized chlorobutadiene (neoprene), for example, have proved to be particularly well suited for the purpose. Other useful materials include for example, polyvinyl chloride, chlorinated naphthalene, chlorinated tricresyl phosphate and the like. Although the exact relationship is not certain, it appears that where a higher degree of chlorination is used less material is required and vice versa. Chlorinated products are those most generally employed because of their availability but use of the other halogens is perfectly feasible. Amounts varying from 5–30% of 40% chlorinated paraffin or its equivalent may be used. As the examples which follow show, a good general practice is to add enough chlorinated material to provide about 3–10% by weight of the padding bath as combined chlorine, available for liberation of HCl at elevated temperatures.

Similarly, the flame-resistant pigment may be varied if so desired. It should, however, be one which not only is compatible with the emulsion but also is colorless or white or only lightly colored so as not to effect adversely the coloration obtained from the color-producing materials. Finally, it must be one which when used with the halogenated material is effective to impart flame-resistance. Such pigments as calcium or magnesium carbonate or the like have been used. Other suggestions include zinc borate, magnesium ammonium phosphate, melamine pyrophosphates and the like. However, finely-powdered antimony oxide has proved generally superior in use and is therefore preferred. From about 5–30% of antimony oxide or its equivalent may be used. It has been found, as the examples show, that in using antimony oxide it should comprise about 8–20% of the emulsion weight. Some adjustment for differing molecular weights of substitutes therefor may be required.

These flame-proofing materials are usually compounded into the final emulsion as a unit by first blending together the chlorinated material and the pigment. In so doing, a small amount of a volatile solvent, usually a hydrocarbon solvent, is used to thin the chlorinated material slightly. Where the emulsifying agent is formed in situ it is well to add at least part of the acidic constituent therefor with the flame-proofing material. A small amount of some soap-forming acidic material such as linseed-oil fatty acids, oleic acid or the like, also is added therewith in such cases. Only a sufficient amount of solvent should be used to impart the requisite fluidity since the principal purpose of this opera-

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tion is to assist in the eventual compounding of the final emulsion and excessive amounts of volatile solvents are neither necessary nor desirable.

Since the coloring pigments have no affinity for the fabrics, it is necessary to provide some binder to effect a pigment-fibre attachment bond. Again the invention has the advantage of not being limited to specific materials. While the binders may be varied they are subject to certain limitations. Because color is important, the binder should be substantially colorless or of a light shade. It should be unconverted, stable against conversion in the emulsion at normal temperatures and capable of deposition with the pigment from the emulsion. If the fabric has had some pretreatment the binder must be one compatible with any residual material therefrom. Preferably, too, it should be easily converted to a water-insoluble form without any appreciable heating beyond that required in drying the fabric to which the emulsion has been applied.

In accordance with the present invention, it has been found that many heat-convertible alkyd resins, particularly drying-oil-modified alkyds are well suited for this purpose as are many amide-aldehyde resins, particularly the alkylated resins such as butylated urea-formaldehyde resin or butylated melamine-formaldehyde resin. Preferably, in order to insure binding while maintaining the optimum flexibility in the finished product, a mixture as of oil-modified alkyd and amide-aldehyde resins is used. As little as 0.5 to as much as 10% of binder resins may be used. As illustrated in the examples below, a good practice consists of using about 1.0–1.5% of the weight of the emulsion as an amide-aldehyde resin and about 2.0–3.0% as an alkyd resin, the total amount of resin present being from about 3–5%.

Since the flame-proofing is not the sole object but rather one of the principal objects, imparting color to the emulsion, and to the products treated therewith, is an important feature. In accordance with the present invention, color is added to the emulsion and eventually applied to the fabric as a finely-divided pigment. Not only does this have the advantage of providing light fastness in a wide range of colors but it obtains this advantage without the necessity for the various processing treatments required when coloring is done by a dyeing. Substantially any solid, finely-divided, colored, light-fast pigment may be used if so desired.

It is probably preferable though not necessary that the coloring pigments be pre-combined with the binding resins as an ink or color paste before being blended into the final emulsion. This may be readily accomplished by treating a mixture of the components in a mixer or on a suitable ink roller mill or the equivalent. Again, as in blending the flame-resisting materials, to assist in forming the emulsifying agent, a small quantity of an acidic soap-forming material such as a fatty acid is added. A basic soap-forming constituent such as a small amount of aqueous ammonia also may be added if so desired to supplement that in the external phase. Further, this may be supplemented as desired by additional emulsifying and/or dispersing agents such as pine oil, terpineol, terpenes and the like, if so desired.

It will be seen, therefore, that the principal feature of the present invention is an oil-in-water type emulsion in which external aqueous medium is usually thickened somewhat to increase its viscosity and assist in maintaining permanent dispersion. Emulsified in the aqueous medium are a suitably chlorinated organic hydrocarbon, a flame-resistant pigment, a resin binder and a coloring pigment or pigments. In addition, thereto, there may be added various supplementary ingredients such as dispersing or emulsifying constituents, additional fire-proofing agents and the like.

While the emulsion as a whole is substantially a stable heterogeneous composition, it does not consist solely of water as the single dispersion medium with a number of individual ingredients separately suspended therein. Rather, there are present one or more dissolved or colloidally suspended ingredients in the water, which "solution" forms the continuous or outer phase. In addition, there are suspended therein at least two separate dispersed phases; one of these contains flame-proofing constituents, i. e., the fire-retarding pigments and the chlorinated hydrocarbon; the other contains the coloring ingredients and the binder or binders. Each of the dispersed phases in and of itself may comprise a continuous phase having dispersed therein one or more ingredients. Each may, if necessary, contain separate agents to maintain the necessary interfaces.

The above appears to be the principal nature of the final emulsion. This is a consequence of the manner in which the emulsion is compounded. Thus the aqueous dispersion medium is first formulated and then there are separately dispersed therein, first the blend containing the flame-proofing ingredients, and second, the blend containing the binder or binders with or without color. There is, of course, a possibility that part of the material, notably from the pigment and binder blend, is not retained within individual droplets which droplets are dispersed in the medium. Rather, a part of the material may migrate from the droplets and be dispersed per se in the aqueous medium. Some such variation is usually found in all such compositions and does not alter the general characteristics of the composition as a heterogeneous oil-in-water emulsion.

The invention is not necessarily limited to the treatment of any particular materials. Its primary intention is for the treatment of textile fabric sheets and the discussion has been primarily concerned therewith. However, the emulsion is equally well-adapted to the treatment of yarn either in running lengths or skeins. It is capable of producing effective coatings of paper. Metallic fabrics may be also effectively treated; but in the latter case, it is desirable to increase the binder content in order to do so. Treatment of such materials is however, of little practical importance except for wire reinforced fabrics since the flame-proofing feature is not required in work in which only metallic fabrics are used.

The invention will be more illustrated in conjunction with the following examples which are intended by way of illustration only, but not by way of limitation. All parts are by weight unless otherwise noted.

Example 1

A stable, oil-in-water type of emulsion to serve as the basis of the mix was prepared by the following procedure. 5 parts of methyl cellulose (4,000 centipoise grade) were suspended in 95 parts of hot water and cooled with slow stirring to 10° C. While continuing the stirring, 20 parts of aqueous ammonia (the specific gravity 0.90) and 970 parts of water were added and the whole

blended to uniformity. To this was added a previously blended mixture of 400 parts of chlorinated paraffin (40–45% chlorine by weight), 400 parts of antimony oxide (325 mesh), 100 parts of hydrocarbon solvent (distillation range 135–175° C. and containing 92% aromatics) and 10 parts of linseed oil fatty acids. When admixture was complete, stirring was continued until the emulsion became smooth.

Simultaneously there was prepared by mechanical stirring a pigmented mix comprising 220 parts of finely ground chromium oxide, 91.5 parts of a 70% solution of an alkyd resin in a pine oil solvent (the alkyd resin being prepared by condensing 148 parts of phthalic anhydride, 97 parts of glycerine, 182 parts of soya-bean fatty acids and 53 parts of castor oil, condensation being carried out at approximately 210–250° C. until the acid number is between 3 and 7), 32 parts of a 50% solution of butylated urea formaldehyde resin in a solvent comprising equal parts of xylol and butanol, (the resin being prepared by refluxing dimethylolurea with excess butanol), 16.4 parts of pine oil, 20 parts of oleic acid, and 20 parts of aqueous ammonia (specific gravity 0.90). This mixture was milled together on a three roller ink mill with tightly adjusted rollers.

The aqueous emulsion and the pigmented mix were blended to uniform consistency by mechanical stirring to produce a smooth pigmented oil-in-water type emulsion. This emulsion was employed by padding onto burlap and Osnaburg fabrics and squeezing the padded fabric to a wet weight increase of about 100% of the original dry weight and then completely drying the treated fabrics. The treated fabrics remained soft and flexible comparing fairly in these properties to the untreated material. The appearance was completely uniform and the fabrics possessed a notably high degree of flame resistance. Continued exposure to severe weathering conditions such as to six months outdoor exposure or the equivalent hours in an Atlas dual-arc weatherometer did not destroy these properties. The above example corresponds to the following formulation:

Component	Per Cent by Weight
Methyl Cellulose	0.21
28% Aqueous Ammonia	1.66
Fatty Acids	1.25
(As Ammonium Soap)	(1.33)
Antimony Oxide	16.60
Chlorinated Paraffin:	
40% Chlorine	16.60
(42±1% real Chlorine)	(6.8–7.15)
Hydrocarbon Solvent	4.15
Pine Oil	1.80
Alkyd resin	2.66
50% Urea Formaldehyde Resin	1.33
Pigment—Chromium Oxide	9.10
Water	44.64
	100.00

Example 2

A basic emulsion was prepared identical with that of Example 1 except that the chlorinated paraffin content was altered to 268 parts of chlorinated paraffin containing approximately 60% of combined chlorine dissolved in 132 parts of the hydrocarbon solvent described in Example 1. At the same time, a pigmented mix was prepared as in Example 1 from 220 parts of chromium oxide pigment, 91.6 parts of the 70% alkyd resin solution of Example 1, 32 parts of the 50% solution of butylated urea formaldehyde resin described in Example 1, 16.4 parts of pine oil, 20 parts of oleic acid, and 20 parts of aqueous ammonia (sp. gr. 0.90). The emulsion and pigment mix were mechanically blended to uniform consistency and as in Example 1 the result was a smooth oil-in-water type emulsion used in padding burlap and Osnaburg fabrics. As in Example 1, a smooth uniform color and high flame resistance were obtained without substantially altering the hand and these desirable properties remain despite continued exposure to severe weather. The above example corresponds to the following formulation:

Component	Per Cent by Weight
Methyl Cellulose	0.21
28% Aqueous Ammonia	1.66
Fatty Acids	1.25
(As Ammonium Soap)	(1.33)
Antimony Oxide	16.60
Chlorinated Paraffin: 60% Chlorine	11.10
Hydrocarbon Solvent	9.65
Pine Oil	1.80
Alkyd Resin	2.66
50% Urea Formaldehyde Resin	1.33
Pigment—Chromium Oxide	9.10
Water	44.64
	100.00

Example 3

183 parts of a 20% solution of an elastomeric chlorobutadiene polymer in a hydrocarbon solvent (boiling at 135°–175° C. and containing 92% aromatic hydrocarbons) were mixed with 73 parts of pulverized antimony oxide (325 mesh), 5 parts of the dried and pulverized precipitate obtained by adding an acidified solution of sodium pyrophosphate to a boiling solution of melamine, 29 parts of chlorinated paraffin containing 72% combined chlorine, 1.8 parts of oleic acid, and 55 parts of hydrocarbon solvent (boiling at 135°–175° C. and containing 92% aromatics).

This mix was added, with continuous agitation, to a uniform aqueous solution of 3.6 parts of methyl cellulose (3,000 centipoise Methocel), 5 parts of 28% aqueous ammonia and 385 parts of water and the agitation continued to form a smooth oil-in-water type emulsion.

Simultaneously there was prepared by mechanical stirring a pigmented mix comprising 10 parts of yellow precipitated iron oxide pigment, 25 parts of the alkyd resin solution described in Example 1, 8 parts of the butylated urea formaldehyde resin solution described in Example 1, 5 parts of pine oil, 5 parts of oleic acid, and 6 parts of aqueous ammonia (sp. g. 0.90). This mixture was milled together on a three roller ink mill with tightly adjusted rollers.

The aqueous emulsion and the pigmented mix were blended to uniform consistency by mechanical stirring to produce a smooth pigmented oil-in-water type emulsion. This emulsion was employed by padding onto burlap and Osnaburg fabrics and squeezing the padded fabric to a wet weight increase of about 100% of the original dry weight and then completely drying the treated fabrics. The treated fabrics remained soft and flexible comparing fairly in these properties to the untreated material. The appearance was completely uniform and the fabrics possessed a notably high degree of flame resistance. Continued exposure to severe weathering conditions such as to six months outdoor exposure or the equivalent hours in an Atlas dual-arc weatherometer did not

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destroy these properties. The above example corresponds to the following formulation:

Component	Per Cent by Weight
Methyl Cellulose	0.45
28% Aqueous Ammonia	1.37
Fatty Acids	0.98
(As Ammonium Soap)	(1.04)
Antimony Oxide	9.14
Chlorinated Paraffin:	
72% Chlorine	3.62
+Chlorobutadiene	4.57
Hydrocarbon Solvent	25.10
Melamine Pyrophosphate	0.63
Pine Oil	1.56
Alkyd Resin	2.19
50% Urea Formaldehyde Resin	1.00
Pigment—Iron Oxide	1.25
Water	48.14
	100.00

I claim:

1. A stable, heterogeneous, oil-in-water type emulsion, adapted for the simultaneous deposition on fabrics from an aqueous medium of fire-resisting, coloring and binding materials, which emulsion is comprised of a continuous dispersion medium comprising water containing a hydrophilic colloid; a dispersed phase comprising a film-forming, substantially colorless fire-resistant, water-insoluble, non-volatile, chlorinated organic compound capable of liberating HCl at elevated temperatures, a colorless, fire-retarding pigment, and a hydrocarbon solvent; a separately dispersed phase comprising water-insoluble organic solvent, at least one coloring pigment and an uncured, heat-convertible, binder resin, selected from the group consisting of (*a*) the drying-oil-modified alkyd resins, (*b*) the organic hydrocarbon solvent-soluble, amide-aldehyde resins and (*c*) mixtures thereof; and a water-soluble soap of a higher fatty acid, the proportions as weight percentages of the total emulsion being 0.1–10% hydrophilic colloid, sufficient chlorinated organic compound to provide from about 2–12% of combined chlorine capable of liberating HCl at elevated temperatures, 5–30% fire-retarding pigment, 0.5–10% binder resin and 0.25–4.0% soap.

2. A composition according to claim 1 in which the hydrophilic colloid is a water-soluble methyl cellulose and the emulsifying agent is an ammonium soap.

3. A composition according to claim 1 in which the dispersed material is substantially all dispersed in sizes not greater than 30 microns.

4. A stable, heterogeneous, oil-in-water-type emulsion, adapted for the simultaneous deposition on fabrics from an aqueous medium of fire-resisting, coloring, and binding materials, which emulsion is comprised of a continuous dispersion medium comprising water containing a hydrophilic colloid; a dispersed phase comprising a film-forming, non-volatile, chlorinated paraffin, finely-divided antimony oxide and a hydrocarbon solvent; a separately dispersed phase comprising water-insoluble organic solvent, at least one coloring pigment and an uncured, heat-convertible, binder resin selected from the group consisting of (*a*) the drying-oil-modified alkyd resins, (*b*) the organic hydrocarbon solvent-soluble amide-aldehyde resins, and (*c*) mixtures thereof; and a water-soluble soap of a higher fatty acid, the proportions as weight percentages of the total emulsion being 0.1–10% hydrophilic colloid, sufficient chlorinated paraffin to provide from about 2–12% of combined chlorine capable of liberating HCl at elevated temperatures, 5–30% antimony oxide, 0.5–10% binder resin and 0.25–4.0% soap.

5. A method of producing a stable, heterogeneous, oil-in-water-type emulsion, adapted for the simultaneous deposition on fabrics from an aqueous medium of fire-resisting, coloring, and binding materials, which comprises the steps of preparing an aqueous medium by dissolving therein 0.1–10% of a hydrophilic colloid, 0.25–4.0% of a water-soluble soap of a higher fatty acid and sufficient alkaline material to maintain an alkaline pH; blending into a smooth paste a mixture comprising sufficient film-forming, substantially colorless, fire-resistant, water-insoluble, non-volatile, chlorinated organic compound to provide from about 2–12% of combined chlorine capable of liberating HCl at elevated temperatures, 5–30% of a colorless fire-retarding pigment and only a sufficient amount of a hydrocarbon solvent to impart fluidity; blending at least one coloring pigment into a smooth paste with a solvent solution of 0.5–10% of an uncured, heat-convertible binder resin, selected from the group consisting of (*a*) the drying-oil-modified alkyd resins, (*b*) the organic hydrocarbon solvent-soluble amide-aldehyde resins and (*c*) mixtures thereof, and separately dispersing the pasted materials into the aqueous medium, the percentages given being weight percentages of the total emulsion.

6. A process according to claim 5 in which the hydrophilic colloid is a water-soluble methyl cellulose and the emulsifying agent is an ammonium soap.

7. A process according to claim 5 in which the dispersed material is substantially all dispersed in sizes not greater than 30 microns.

8. A process according to claim 5 in which the emulsifying agent is an ammonium soap of a higher fatty acid formed in situ by adding the acidic component to the aqueous medium and adding the basic constituent with the dispersed phase.

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