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LAMINATED GLASS

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The present invention relates to safety glass and more particularly to plastic products for use as intermediate sheets or layers between the glass sheets of such laminated glass.

The imperfections of present-day safety glass are well known. Changes such as darkening, loss of transparency, crystallization and embrittlement of the intermediate plastic sheets of safety glass in normal use occur after short periods. It is recognized that these imperfections of the intermediate sheet are not entirely inherent in the cellulose nitrate or acetate or other material that is the base of the plastic composition; rather, the imperfections are largely attributable to those substances, particularly plasticizers, which are added to modify the properties of the base to impart to the composition suitable characteristics which permits its use for safety glass.

It is an object of the present invention to provide a plastic composition for use as the intermediate sheet in safety glass production, which composition is improved particularly in regard to flexibility at low temperatures. Thus, it is an object of the invention to provide a modifying agent for use with the customary plastic bases of such intermediate sheets, which modifying agent imparts to the plastic base an exceptional flexibility at low temperatures and which agent is characterized by great stability to light, water resistance, retentivity in the plastic composition, and exceptional miscibility with the other components of the plastic composition. Furthermore, the plastic sheet must possess permanently brilliant transparency and be smooth and tough.

Other objects and advantages of the invention will be more apparent from the description which follows.

It is known that when alkyl phosphates, such as tributyl phosphate, are used as plasticizers, discoloration by the action of light is to a large extent prevented. The proportion of such a plasticizer which can be retained in any individual plastic composition, however, is rather limited.

The present invention is based in part on the discovery that certain alkyl phosphates, for example, tributyl phosphate, impart to cellulose acetate, cellulose nitrate and other plastic substances an extraordinary degree of flexibility in

comparison with the amount of alkyl phosphate added and that this flexibility is retained at low temperatures. However, the proportion of alkyl phosphate which can be retained in such compositions is too small to produce films of satisfactory flexibility for many purposes. It was found that when tributyl phosphate is admixed with an equal proportion of diethyl phthalate or other plasticizer a greater proportion of the mixture can be incorporated into and retained by the composition without any sacrifice of the desirable light resistance and flexibility at low temperatures inherent in the alkyl phosphate and that products of greater flexibility result than can be obtained without this admixture. Thus the presence of the alkyl phosphates has been found to have a synergistic effect or action with respect to the plastic when used in conjunction with alkyl phthalate and aryl sulfonamide plasticizers. This effect is illustrated in the results of tests which are set forth hereinafter. Whereas compositions containing dimethyl phthalate are not especially flexible at low temperatures, the addition of tributyl phosphate imparts this property thereto. Thus, in admixture the tributyl phosphate appears to transmit to other plasticizers not especially characterized thereby, an improved flexibility without impairing other desirable qualities.

Several methods of applying the discovery, which are suggestive of many other applications, are illustrated in greater detail in the following description.

The following examples are typical of the effect produced on a resin resulting from the condensation of formaldehyde with a partially hydrolyzed vinyl ester polymer. A commercial resin of this type, known as "Formvar," was used with the indicated parts by weight of the various plasticizing substances and mixtures; the proportions represent parts by weight of the substances to 100 parts of the resin. Uniform thin sheets of the plastic composition were made, the sheets being approximately 0.025 inch in thickness, and these were subjected to bending tests while at a temperature of -20°F. (-29°C.). The number of bends, each bend consisting of a bend through an angle of 180° and back to the original position, which the composition could withstand without cracking, is taken to be a measure of the

flexibility of the composition at that temperature.

Table I—"Formvar" resin

		Bends at -20° F.		
1. Tributyl phosphate 60-----	125-164	5	31. Tributyl phosphate 75 diethyl phthalate 75-----	300-426
2. Tributyl phosphate 75-----	118-196		32. Tributyl phosphate 75 dimethyl phthalate 37½ diethyl phthalate 37½-----	400-650
3. Dimethyl phthalate 60-----	33		33. Tributyl phosphate 50 methyl phthalyl ethyl glycolate 100-----	203-293
4. Dimethyl phthalate 75-----	15-26		34. Tributyl phosphate 75 methyl phthalyl ethyl glycolate 75-----	215-388
5. Diethyl phthalate 60-----	50-74	10	35. Tributyl phosphate 75 methyl phthalyl ethyl glycolate 37½ ethyl phthalyl ethyl glycolate 37½-----	70-98
6. Diethyl phthalate 75-----	95-124		36. Tributyl phosphate 37½ methyl phthalyl ethyl glycolate 75 ethyl phthalyl ethyl glycolate 37½-----	180
7. Tributyl phosphate 30 dimethyl phthalate 30-----	28-32		37. Tributyl phosphate 37½ methyl phthalyl ethyl glycolate 37½ ethyl phthalyl ethyl glycolate 75-----	45-56
8. Tributyl phosphate 37½ dimethyl phthalate 37½-----	125-146	15	38. Tributyl phosphate 37½ methyl phthalyl ethyl glycolate 75 diethyl phthalate 37½-----	70-144
9. Tributyl phosphate 30 diethyl phthalate 30-----	40-58		39. Tributyl phosphate 75 ethyl phthalyl ethyl glycolate 75-----	5
10. Tributyl phosphate 37½ diethyl phthalate 37½-----	600-1170	20	40. Tributyl phosphate 75 methyl phthalyl ethyl glycolate 37½ diethyl phthalate 37½-----	230-410
11. Tributyl phosphate 34 diethyl phthalate 40-----	120-218		41. Tributyl phosphate 100 dimethyl phthalate 50-----	1050-1229
12. Tributyl phosphate 37½ dimethyl phthalate 18¾ diethyl phthalate 18¾-----	190-232	5	42. Tributyl phosphate 50 dimethyl phthalate 100-----	460-664
13. Methyl phthalyl ethyl glycolate 60--	1	25	43. Tributyl phosphate 100 diethyl phthalate 50-----	375-428
14. Methyl phthalyl ethyl glycolate 75--	18-23		35 44. Tributyl phosphate 50 diethyl phthalate 100-----	208-361
15. Tributyl phosphate 30 methyl phthalyl ethyl glycolate 30-----	60-74	4	45. Tributyl phosphate 100 ethyl phthalyl ethyl glycolate 50-----	20-106
16. Tributyl phosphate 37½ methyl phthalyl ethyl glycolate 37½-----	4	30	46. Tributyl phosphate 50 ethyl phthalyl ethyl glycolate 100-----	150-206
17. Ethyl phthalyl ethyl glycolate 60--	3		47. Tributyl phosphate 100 methyl phthalyl ethyl glycolate 100-----	460-556
18. Ethyl phthalyl ethyl glycolate 75--	28-34		48. Dimethyl phthalate 50 methyl phthalyl ethyl glycolate 100-----	3
19. Tributyl phosphate 30 ethyl phthalyl ethyl glycolate 30-----	90-138	45	49. Dimethyl phthalate 75 methyl phthalyl ethyl glycolate 75-----	5
20. Tributyl phosphate 37½ ethyl phthalyl ethyl glycolate 37½-----		1	50. Dimethyl phthalate 150-----	1

In all the above examples the light resistance, water resistance, fire resistance, flexibility at room temperature (20° C.), and transparency were exceptionally good. In compositions numbered 1 and 2 there was slight exudation showing a slight lack of retentivity of the tributyl phosphate. Very slight exudation was noted also in compositions numbered 10, 16 and 20. It will be noted that the flexibility at the low temperature (number of bends) of the mixture with tributyl phosphate is greater in every case than the composition without the tributyl phosphate and in most cases is greater than the flexibility which would result from the use of tributyl phosphate alone.

The following table represents typical results to be obtained when cellulose acetate is treated according to the invention. The conclusions are similar to those above, that is, the flexibility at room temperature is good, and the light resistance, water resistance, fire resistance, transparency, brilliance and such characteristics are exceptionally good.

Table II—Cellulose acetate

		Bends at -20° F.
21. Dimethyl phthalate 100-----	21	
22. Dimethyl phthalate 125-----	1	
23. Dimethyl phthalate 150-----	65-94	
24. Diethyl phthalate 125-----	1	65
25. Diethyl phthalate 150-----	25-68	
26. Methyl phthalyl ethyl glycolate 100-----	1	
27. Ethyl phthalyl ethyl glycolate 100--	1	
28. Dimethyl phthalate 45 diethyl phthalate 55-----	1	70
29. Dimethyl phthalate 56¼ diethyl phthalate 68¾-----	3	
30. Dimethyl phthalate 67½ diethyl phthalate 82½-----	70-118	75

It is to be observed that mixtures not containing alkyl phosphates (compositions numbered 48, 49 and 50) do not show the advantageous effects produced when alkyl phosphates are admixed. Compositions numbered 24, 25 and 31 sweated, this indicating a slight lack of retentivity.

The tributyl phosphate described hereinabove is the normal butyl derivative and is particularly useful as the plasticizer in intermediate plastic sheets in the production of safety glass. On the other hand, triethyl phosphate is characterized by not as great an ability to impart flexibility which is permanent at low temperatures to the resulting plastic composition, but it can be used with some success in partially replacing tributyl phosphate in some compositions. In the compositions described it is possible to substitute partially or completely the tributyl phosphate by other isomeric tributyl phosphates, or by tripropyl, triamyl, and trihexyl derivatives. Triethyl phosphate is too soluble in water and too easily decomposed to be entirely satisfactory for the uses contemplated herein, especially when used alone or to replace predominant proportions of tributyl or higher alkyl phosphates. Triphenyl or tricresyl phosphates are not as advantageous for use in accordance with this invention as are

the alkyl phosphates; cellulosic compositions made therewith are characterized by poor light stability and poor flexibility at low temperatures.

The plasticizers which can be used in the same manner as diethyl phthalate as specified above, that is, those which are used in admixture with the alkyl phosphates to produce the advantageous results of this invention, include such varied plasticizers as phthalates, for example, dibutyl and diamyl phthalate; glycolates, for example, methyl or ethyl phthalyl ethyl glycolate; toluenesulfonamides and similar plasticizers. The plasticizers are preferably those which are light stable and miscible with the alkyl phosphate as well as with the plastic.

The range of plastic substances to which the plasticizers of the invention are adapted is limited only by the compatibility of the plasticizer with the plastic. For making safety glass the industry is largely restricted to the utilization of cellulose acetate, smaller amounts of cellulose nitrate and the newer vinyl resins such, for example, as "Formvar" and "Gelva." To the plasticization of these materials the invention is especially applicable.

The proportions of any particular plasticizer mixture which are used in the preparation of the plastic compositions of the invention may be varied considerably. Preferably about equal parts of tributyl phosphate and diethyl phthalate are used but as little as 10 parts of tributyl phosphate to 90 parts of diethyl phthalate are satisfactory for many purposes. On the other extreme, 90 parts of tributyl phosphate and 10 parts of diethyl phthalate are usable to obtain other ranges of properties. With other plasticizing substances similar variations of proportions can be made to produce compositions for specific purposes.

The method of incorporating the plasticizer into the plastic composition presents no features new to the art. Any of the standard methods, such as kneading with or without the aid of heat, solution in mutual solvents or similar procedures may be used.

Inasmuch as the specification comprises preferred embodiments of the invention it is to be understood that the invention is not limited thereto and that changes and modifications may be made therein without departing substantially from the invention, which is defined in the appended claims.

I claim:

1. The method of increasing the compatibility and retentivity of a trialkyl phosphate, the alkyl radicals of which contain more than two and not more than six carbon atoms, with an organic plastic substance characterized by a plurality of C—O—C linkages and selected from the group consisting of cellulose derivatives, vinyl ester and vinyl acetal resins, and at the same time producing a synergistic increase in the flexibility at subatmospheric temperature conditions of such a composition, which comprises incorporating uniformly with said composition a modifying substance consisting of a neutral alkyl phthalate ester selected from the group consisting of neutral dialkyl phthalate esters having not more than five carbon atoms in each alkyl group and neutral alkyl esters of phthalyl glycolic acid having not more than two carbon atoms in each alkyl group.

2. A plastic composition embodying an organic plastic substance characterized by a plurality of C—O—C linkages and selected from the

group consisting of cellulose derivatives, vinyl ester and vinyl acetal resins, and embodying a mixture of two plasticizing substances, one of which is a trialkyl phosphate, the alkyl radicals of which contain more than two but not more than six carbon atoms, and the other of which is a phthalate ester selected from the group consisting of neutral dialkyl phthalate esters having not more than five carbon atoms in each alkyl group and neutral alkyl esters of phthalyl glycolic acid having not more than two carbon atoms in each alkyl group, whereby a degree of flexibility is imparted to the composition at subnormal temperature conditions as a result of the synergistic action of the two modifying substances that is not attainable by means of the presence in the composition of the phthalate ester modifying substance without the trialkyl phosphate in a proportion corresponding to the total proportion of the mixture of the two modifying substances.

3. A plastic composition embodying an organic plastic substance characterized by a plurality of C—O—C linkages and selected from the group consisting of cellulose derivatives, vinyl ester and vinyl acetal resins, and embodying a trialkyl phosphate, the alkyl radicals of which contain more than two but not more than six carbon atoms, in a proportion corresponding to more than 30 parts by weight of the trialkyl phosphate to 100 parts by weight of the organic plastic substance, and embodying a phthalate ester selected from the group consisting of neutral dialkyl phthalate esters having not more than five carbon atoms in each alkyl group and neutral alkyl esters of phthalyl glycolic acid having not more than two carbon atoms in each alkyl group, in a proportion sufficient to impart to the plastic composition a degree of flexibility under subnormal temperature conditions without exudation of the trialkyl phosphate that is not attainable by means of the presence in the composition of the phthalate ester without the trialkyl phosphate in a proportion corresponding to the total proportion of the two plasticizing substances.

4. A plastic composition embodying a vinyl acetal resin and a mixture of two modifying substances, one of which is a neutral dialkyl phthalate ester having not more than five carbon atoms in each alkyl group, and the other of which is a trialkyl phosphate, the alkyl radicals of which latter substance contain more than two but not more than six carbon atoms, whereby a degree of flexibility under subnormal temperature conditions is imparted to the composition as a result of the synergistic action of the two modifying substances that is not attainable by means of the presence in the composition of the neutral alkyl phthalate ester modifying substance without the trialkyl phosphate in a proportion corresponding to the total proportion of the mixture of the two modifying substances.

5. A plastic composition embodying a polyvinyl acetal resin and embodying a mixture of two plasticizing substances, one of which is a trialkyl phosphate, the alkyl radicals of which contain more than two but not more than six carbon atoms, in a proportion corresponding to from 30 to 37½ parts by weight to 100 parts by weight of the polyvinyl acetal resin, and the other of which is a phthalate ester selected from the group consisting of neutral dialkyl phthalate esters having not more than five carbon atoms in each alkyl group and neutral esters of phthalyl

glycolic acid having not more than two carbon atoms in each alkyl group, in a proportion corresponding to from 30 to 37½ parts by weight to 100 parts by weight of the polyvinyl acetal resin.

6. A plastic composition embodying a cellulose derivative and a mixture of two modifying substances, one of which is a neutral dialkyl phthalate ester having not more than five carbon atoms in each alkyl group, and the other of which is a trialkyl phosphate, the alkyl radicals of which latter substance contain more than two but not more than six carbon atoms, whereby a degree of flexibility under subnormal temperature conditions is imparted to the composition as a result of the synergistic action of the two modifying substances that is not attainable by means of the presence in the composition of the neutral alkyl phthalate ester modifying substance without the trialkyl phosphate in a proportion corresponding to the total proportion of the mixture of the two modifying substances.

7. A plastic composition embodying cellulose acetate and embodying a mixture of two plasticizing substances, one of which is a trialkyl phosphate, the alkyl radicals of which contain more than two but not more than six carbon atoms, in a proportion corresponding to more than 50 parts by weight of the trialkyl phosphate to 100 parts of the cellulose acetate and the other of which is a phthalate ester selected from the group consisting of neutral dialkyl phthalate esters having not more than five carbon atoms in each alkyl group and neutral esters of phthalyl glycolic acid having not more than two carbon atoms in each alkyl group, in a proportion cor-

responding to more than 50 parts by weight of the phthalate ester to 100 parts by weight of the cellulose acetate.

8. Safety glass including in combination a plurality of sheets of glass bonded together through the medium of a plastic composition as defined in claim 2.

9. Safety glass including in combination a plurality of sheets of glass bonded together through the medium of a plastic composition as defined in claim 3.

10. Safety glass including in combination a plurality of sheets of glass bonded together through the medium of a plastic composition as defined in claim 4.

11. Safety glass including in combination a plurality of sheets of glass bonded together through the medium of a plastic composition as defined in claim 5.

12. Safety glass including in combination a plurality of sheets of glass bonded together through the medium of a plastic composition as defined in claim 6.

13. Safety glass including in combination a plurality of sheets of glass bonded through the medium of a plastic composition as defined in claim 7.

14. A transparent, rubbery sheet comprising 100 parts of a polyvinyl formaldehyde acetal resin and, as an elasticizer therefor, at least 60 parts, approximately, of an alkyl phthalyl ethyl glycolate in which the alkyl group contains less than 3 carbon atoms.

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CERTIFICATE OF CORRECTION.

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July 21, 1942.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 48, for the word "import" read --impart--; page 2, first column, line 19, for the numeral "34" read --35--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of August, A. D. 1942.

Henry Van Arsdale,

Acting Commissioner of Patents.

(Seal)