

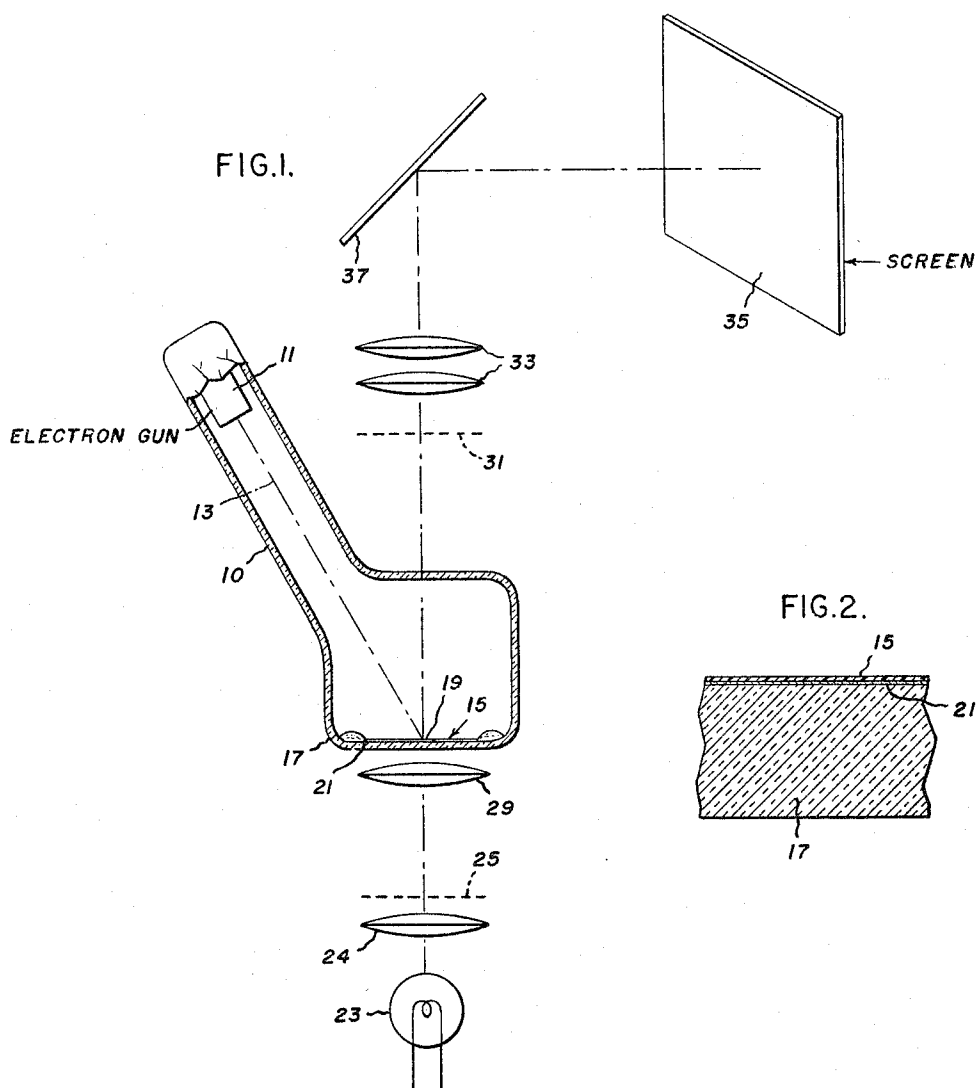
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PROJECTION SYSTEM

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3,288,927

PROJECTION SYSTEM

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This invention relates to projection systems of the electronic type. More particularly, it relates to such projection systems having a container with a conducting interior and a deformable medium in the container that decreases in resistivity with decreases in thickness in the presence of an electrical charge on the surface of the medium, the medium being the polymeric reaction product of benzyl chloride and aromatic compounds.

There is described in U.S. Patent No. 2,943,147, June 28, 1960, assigned to the same assignee as the present invention, a projection system of the above type employing a deformable medium having a high resistivity which is responsive to a velocity modulated electron beam. Generally speaking, this projection system, which is illustrated in FIG. 1 of the drawing, comprises an evacuated glass envelope 10 containing an electron gun 11 for producing an electron beam 13 deflecting the beam in a rectangular raster over the surface of a light transmitting deformable medium 15 which is within a portion 17 of the transparent container. An enlarged view of this portion of the assembly is shown in FIG. 2. The beam 13 is preferably velocity-modulated by a television signal applied to the deflection means (not shown) in the electron gun 11. Deformable medium 15 has a central portion 19 of decreased thickness which is coincident with the raster area of beam 13 produced by electrons from beam 13 which are attracted to a conducting coating 21 on the inner surface of the container portion 17. These same electrons also produce deformations in the surface of the deformable medium 15 and the amplitudes of these deformations are a function of the number of electrons deposited by the beam 13 at the various points on the surface of medium 15. Thus, the amplitudes of these deformations are a function of the modulated electron beam 13.

The deformations on the surface of medium 15 are utilized to diffract light from a source 23 in an optical system which includes a lens 24 which projects an image of light source 23 on the surface of medium 15 through a bar and slit system 25. Another lens 29 images the slits of system 25 on the bars of another bar and slit system 31 if there are no deformations on the surface of deformable medium 15. However, any deformations on such surface diffract the transient light so that it passes through the slits in the system 31 with an intensity that corresponds to the amplitudes of the deformations and hence the amplitudes of the applied modulating signal such as a television signal. The light passing through system 29 is imaged by a projection lens 33 on screen 35 by means of mirror 37.

If a conventional deformable medium is utilized at 15 in the illustrated system, the average charge density produces a force on the medium 15 that overcomes the surface tension from the excess medium outside the raster area and decreases the portion 19 of medium 15 to zero thickness. Under such conditions, no deformations can be formed and the system becomes inoperative until the medium is replaced. The above patent teaches that if the medium has the property of decreasing in resistivity with decreasing thickness, portion 19 does not decrease to zero thickness under the pressure of the charges but maintains a thickness which is a function of the magnitude of charge density on the surface of the medium 15. With decrease in resistivity, the time constant is decreased for the passage of leakage current from the surface of deformable medium 15 to the conducting coating beneath it. This

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results in an increase in leakage current, decreasing the charge density on the surface of the medium 15 and somewhat relieving the pressure. Eventually, an equilibrium condition is reached in which the pressure from the charges on the surface of the medium equals the pressure from the surface tension on the excess medium surrounding the raster at which the thickness at this equilibrium condition is maintained. The charge density on the surface of the medium never decreases to zero because of such leakage because it is continually being replaced by electrons from beam 13.

The deformable composition described in the aforesaid patent, U.S. 2,943,147, as suitable for the medium are required to be transparent, be capable of withstanding electron bombardment without significant decomposition, have a viscosity at the operating temperature (between about 25° C. and 150° C.) of approximately 100 to 50,000 centistokes, and the deformable composition must not decompose the conducting coating. The medium must also have a volume resistivity that varies within the range of approximately 10^{11} to 10^{14} ohms-cm., with the average resistivity at the stable thickness being approximately 10^{11} ohms-cm.

Among the deformable media or fluids described in this patent are, for instance, beeswax, methyl silicone fluids, methyl silicone fluids containing up to 5% of phenyl silicones, methylphenyl silicones containing an average of two methyl and phenyl groups per silicon atom in which the mole ratio of methyl groups to silicon atoms is greater than 0 and less than 2, etc. However, it has been found that these deformable fluids are not as stable as one would desire because under the influence of an electron beam, the deformable medium or deformable fluids tends to increase in viscosity and with continued use of the projection system described above, the viscosity increases to a point where gel particles begin to form and ultimately the deformable medium gels. This means that the apparatus can no longer be used with that particular deformable medium.

From the above, it will be apparent that there is a definite need for materials which can be used as medium 15 which are characterized by a desirably low rate of thickening under the radiation effects of electrons from beam 13. At the same time, such materials should be characterized by good writing behavior under the action of electrons. They should have a good general working viscosity, that is, they should not be too thin. They should have a suitably low vapor pressure and they should be economical.

It is therefore a principal object of the invention to provide materials which are possessed of such desirable qualities.

It has been unexpectedly found that the polymeric Friedel-Crafts reaction products of chloroalkylated aromatic materials, such as benzyl chloride, with other aromatic hydrocarbons admirably fit the above characteristics and provide a deformable medium which is possessed of long working life. Specifically, such materials which have a viscosity of at least 100 centistokes (cs.) at 25° C. and have other desirable qualities have been found to be useful. Materials with a lower viscosity have an undesirably high vapor pressure.

Benzyl chloride is the preferred chloroalkylated material used herein. It will, of course, be appreciated that other halo-substituted benzyl materials of the above description can be used such as the iodo- and bromo-substituted materials. However, the chloro-substituted materials are preferred from the point of view of cost and ready availability as well as from the point of view of easier processing.

Among the aromatic hydrocarbons which can be used are benzene, toluene, benzyl toluene and diphenyl meth-

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ane. It is important that no alkyl groups higher than methyl groups be included as ring substituents in the aromatic material in order that gasification be held to a minimum under electron irradiation. Blends of such materials can also be used. Aluminum chloride is preferred as the catalyst material but other materials, such as zinc chloride, ferric chloride, mercury zinc amalgam, mercury sodium amalgam as well as various silicate materials, can be used.

Generally speaking, in forming the present materials preferably from about 0.8 to 3 moles of chloromethylated aromatic material, such as benzyl chloride, are used for each mole or aromatic hydrocarbon. Broadly speaking, from about 0.1 to about 10 moles of chloromethylated material is used for each mole of aromatic hydrocarbon.

Example 1

Dry toluene in the amount of 460 grams (5 moles) was stirred and slowly heated with 20 grams of a 1:1 by weight powdered mixture of zinc chloride and magnesium Celkate while benzyl chloride in the amount of 949 grams (7.5 moles) was added dropwise for about four hours, the temperature meanwhile being raised from about 45° C. to 89° C. Celkate is a synthetic magnesium silicate material made by the Johns-Manville Corporation. The batch was then stirred for about 16 hours at 90–93° C. after which the reaction was complete as judged by the absence of HCl. Next, a filtering aid was added, and 300 cc. of toluene also, for its thinning effect, after which the batch was filtered and shaken with 250 cc. of about 30% caustic soda. The organic product layer was dried, filtered and distilled. After removing the excess and unreacted toluene, intermediate fractions were distilled off. The following table shows the fractions obtained, their principal composition, their weight, and yields (in mole percent) based on the starting quantity of benzyl chloride entering their composition.

	Percent
Monobenzyl toluene, 264.7 grams	19.4
Dibenzyl toluene, 285 grams	28.0
Tri- and tetrabenzyl toluene, 285 grams	34.2
Undistilled residue, assumed pentatoluene, 91 grams	11.2
Total recovery	92.8

Example 2

To a stirred mixture of 1560 grams (17 moles) of dry toluene and 25 grams $AlCl_3$ cooled with an ice-HCl bath, there were added 2365 grams (18.7 moles) benzyl chloride dropwise over a period of about one hour with reaction temperature maintained at 0 to 12° C. The reaction mixture was neutralized with 300 ml. dilute hydrochloric acid, the organic layer separated out and extracted again with dilute HCl; aqueous layer discarded, and organic layer shaken thoroughly with 40% potassium hydroxide solution. Organic layer removed from basic solution, dried over anhydrous K_2CO_3 plus Celkate, filtered and distilled gave the fractions described below:

Fraction	Boiling Range, ° C. (mm. Hg)	Refractive Index, 25° C.	Viscosity, cs. @ 25° C.	Weight, Grams
1	146–182 (10)	1.5692	-----	818
2	190–298 (10)	1.5992	-----	764
3	203–320 (0.04)	1.6167	2,200	672
4	278—>400 (0.5)	-----	-----	258
Pot residue	-----	-----	-----	26

Fractions 3 and 4 and the pot residue provided useful materials, the lower fractions having too low a viscosity.

Example 3

A reaction was carried out between 830 grams (9 moles) toluene, 2530 grams (20 moles) benzyl chloride and 15 grams aluminum chloride at 6 to 18° C. over a two-hour period. Following acid neutralization, KOH extraction,

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drying and decolorizing with K_2CO_3 and Celkate and filtration, the reaction product was distilled with the following results:

Fraction	Boiling Range, ° C. (mm. Hg)	Refractive Index, 25° C.	Viscosity, cs. @ 25° C.	Weight, Grams
1	155–245 (10)	1.5733	-----	565
2	242–282 (10)	1.6014	-----	479
3	186–306 (0.03)	1.6200	4,896	831
Pot residue	-----	-----	-----	581

Fraction 3 and the pot residue provided useful materials, Fractions 1 and 2 having too low a viscosity. The pot residue of this example was subjected to electron irradiation with a 1500 kv. resonant transformer at a current input of 200–500 microamperes at a dose of $20\text{--}50 \times 10^6$ roentgens/minute to a total dose of 2000 megaroentgens. The total number of molecules of gas per 100 electron volts absorbed was 0.079. The viscosity in centistokes prior to irradiation measured at 100° C. was 255 and after irradiation the viscosity at 100° C. was 670. The very low gas value and the small change in viscosity under the above accelerated test conditions show conclusively the eminent suitability of these compositions as a deformable medium in a projection system of the present type. When such compositions are placed in the projection system, clear images are obtained and the fluid can be used over long periods of time without any apparent evidence of either degradation or gelation of the deformable medium.

Example 4

A reaction carried out as in Example 2 between 414 grams (4.5 moles) toluene, 1253 grams (10 moles) benzyl chloride and 8 grams $AlCl_3$ proceeded at 11 to 18° C. over 1.4 hours. The usual washing and adsorbent procedure afforded a filtrate which on distillation gave the following cuts:

Fraction	Boiling Range, ° C. (mm. Hg)	Refractive Index, 25° C.	Viscosity, cs. @ 25° C.	Weight, Grams
1	86–160 (0.1)	1.5710	-----	151
2	160–222 (0.005)	1.5985	-----	216
3(a)	239–252 (0.001)	1.6085	105	40
3(b)	252–266 (0.005)	1.6129	252	39
3(c)	266 (0.006)	1.6137	304	42
3(d)	266 (0.01)	1.6140	370	40
3(e)	266–288 (0.01)	1.6164	721	41
3(f)	288–304 (0.012)	1.6211	3,740	43
3(g)	304–315 (0.024)	1.6221	5,688	43
3(h)	315–322 (0.038)	1.6236	8,000	43
3(i)	322–333 (0.065)	1.6263	32,500	40
3(j)	333–357 (0.25)	1.6276	62,000	43
3(k)	320–332 (0.0004)	1.6325	480,000	43
3(l)	333–338 (0.0004)	1.6346	1,000,000	40
3(m)	340–355 (0.0004)	1.6356	4,800,000	46
3(o)	357–376 (0.0005)	1.6383	12,500,000	44
3(p)	382–399 (0.001)	1.641	100,000,000	46

Example 5

A mixture of 234 grams (3 moles) dry benzene and 4 to 5 grams aluminum chloride was stirred and cooled to 19° C. Added dropwise over about two hours were 304 grams (2.4 moles) benzyl chloride while maintaining the temperature at 11 to 24° C. The reaction mixture was neutralized and the aqueous layer discarded. The organic layer was then extracted twice with hot 40% KOH solution and twice with 7% H_3BO_3 in H_2SO_4 and placed over anhydrous K_2CO_3 —Celkate. Filtration and distillation gave the cuts noted below:

Fraction	Boiling Range, ° C. (mm. Hg)	Refractive Index, 25° C.	Viscosity, cs. @ 25° C.	Weight, Grams
1	122–134 (10)	1.5750	-----	105
2	146–277 (10)	1.6017	15	78
3	190–316 (0.01)	1.6226	301	87
Pot residue	>316 (0.01)	-----	-----	34

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Fraction 3 with a volume resistivity of 6.9×10^{13} ohm-cm. as well as the pot residue provided good media for the present purpose.

Example 6

There were reacted 117 grams (1.5 mole) benzene, 380 grams (3 moles) benzyl chloride and 4 grams AlCl_3 carried out as in Example 5 over 2.1 hours and at 15 to 28° C. gave after the usual workup the following cuts on distillation.

Fraction	Boiling Range, ° C. (mm. Hg)	Refractive Index, 25° C.	Viscosity, cs. @ 25° C.	Weight, Grams
1.....	122-142 (10)	1.5738	-----	54
2.....	160-266 (10)	1.6013	-----	53
3.....	188-312 (0.03)	1.6237	377	74
Pot residue.....	>312 (0.03)	-----	-----	138

Fraction 3 with a volume resistivity of 1.8×10^{15} ohm-cm. as well as the pot residue provided good media.

Example 7

As in Example 5, 78 grams (1 mole) benzene, 380 grams (3 moles) benzyl chloride and 4 grams AlCl_3 (anhydrous) were reacted. Normal workup of the reaction mixture gave on distillation the following products:

Fraction	Boiling Range, ° C. (mm. Hg)	Refractive Index, 25° C.	Viscosity, cs. @ 25° C.	Weight, Grams
1.....	123-128 (10)	1.5734	-----	19
2.....	130-245 (10)	1.5992	-----	28
3.....	193-314 (0.05)	1.6234	512	52
Pot residue.....	>314 (0.05)	-----	-----	150

Fraction 3 with a volume resistivity of 2.0×10^{15} ohm-cm. and the pot residue proved to be useful writing media.

Example 8

This illustrates the preparation of polybenzyl-o-xylene. A mixture of 318 grams (3 moles) dry o-xylene and 4 to 5 grams AlCl_3 (anhydrous) were cooled to 0° C. To the stirred pot were added 494 grams (3.9 moles) benzyl chloride over 0.7 hour at -2 to +2° C. Evolution of HCl gas stopped quickly and the dark red reaction mixture was neutralized by stirring in 150 ml. dilute HCl acid. The aqueous layer was discarded and the organic product again washed with dilute HCl, followed by two extractions with hot 40% KOH solution. Organic layer was then stirred with anhydrous K_2CO_3 and Celkate and filtered. Distillation productd the following fractions:

Fraction	Boiling Range, ° C. (mm. Hg)	Refractive Index, 25° C.	Viscosity, cs. @ 25° C.	Weight, Grams
1.....	28-48 (15)	1.4719	-----	72
2.....	130-188 (10)	1.5694	-----	208
3.....	190-251 (10)	1.5971	-----	220
4.....	234-300 (0.012)	1.6124	5,700	110
5.....	212-350 (0.0001)	1.6272	3.5×10^7	25

Example 9

The synthesis of polybenzyltoluene from the reaction of benzyl chloride with benzyl toluene is demonstrated herein. Benzyl toluene (5460 grams, 30 moles) recovered from previous benzylations and anhydrous AlCl_3 (45 grams) were mixed and cooled to -3° C. To the resulting red-orange solution were added 3800 grams (30 moles) dry benzyl chloride over two hours and at -3 to +5° C. Following neutralization of the mixture with one liter of dilute HCl acid and a subsequent dilute HCl acid wash, the organic layer was stirred with hot 40% KOH solution, the basic layer discarded and the

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product treated with anhydrous K_2CO_3 and Celkate. Filtration and then distillation afforded the following cuts:

Fraction	Boiling Range, ° C. (mm. Hg)	Refractive Index, 25° C.	Viscosity, cs. @ 25° C.	Weight, Grams
1.....	114-175 (10)	1.5703	-----	1,577
2.....	172-275 (10)	1.5981	-----	2,100
3.....	164-345 (0.15)	1.6771	828	2,335
Pot residue.....	>345 (0.15)	-----	-----	1,388

Fraction 3 and the pot residue were good media. This example shows also that yields of polybenzylated aromatics can be significantly increased by successive benzylations of low molecular weight by-products. Thus, the above Fraction 3 was further stripped into a usable valve fluid of 1738 cs. (25° C.) and of very good color.

Example 10

To eliminate possible oxidation and other undesirable side reactions in the polybenzyltoluene synthesis, the usual reaction was carried out under a dry nitrogen blanket and this is illustrated in the following example. The reaction vessel was flushed for one hour with N_2 scrubbed successively by pyrogallol, concentrated H_2SO_4 , 10-X molecular sieve and a dibenzyltoluene bubbler. With a slow stream of N_2 flowing through, the vessel was charged with 3015 grams (33 moles) dry toluene and 40 to 45 grams AlCl_3 (anhydrous) and the mixture cooled to 0° C. Added over a period of 1.5 hours were 6260 grams (49.5 moles) of freshly distilled benzyl chloride with reaction maintained at -7 to 0° C. Following the usual neutralization with dilute HCl acid (twice), extraction with hot 40% KOH solution, treatment with anhydrous K_2CO_3 and Celkate and filtration, the organic product was distilled giving, after removal of excess toluene, the cuts cited below:

Fraction	Boiling Range, ° C. (mm. Hg)	Refractive Index, 25° C.	Viscosity, cs. @ 25° C.	Weight, Grams
1.....	69-160 (10)	1.5696	-----	1,512
2.....	170-267 (10)	1.5970	-----	1,710
3.....	180-331 (0.04)	1.6178	1,041	1,948
Pot residue.....	>331 (0.04)	-----	-----	958

Fraction 3 and the pot residue were useful media. After the usual stripping and processing a fluid of 1792 cs. was obtained with a very pale blue fluorescence and one of the lightest yellow colors yet realized.

Example 11

This again illustrates the preparation of polybenzyltoluene. A reactor was charged with 12,060 grams (132 moles) dry toluene and 100 grams AlCl_3 and the mixture stirred and cooled. On reaching a temperature of 3° C., the addition of 25,040 grams (198 moles) of benzyl chloride was started and carried out over three hours up to a final temperature of 10° C. The reaction was stirred an additional 0.75 hour, neutralized with dilute HCl acid and the product stirred twice with two and four liter portions of hot 30% KOH solution and treated with 1200 grams anhydrous K_2CO_3 and 400 grams Celkate. After filtration a second treatment with 700 grams Celkate was performed. Filtration gave a straw colored fluid from which excess toluene was stripped. Distillation then gave the following cuts:

Fraction	Boiling Range, ° C. (mm. Hg)	Refractive Index, 25° C.	Viscosity, cs. @ 25° C.	Weight, Grams
1.....	85-214 (10)	1.5693	3.4	6,307
2.....	84-254 (0.01)	1.5984	27.4	6,342
3.....	133-307 (0.001)	-----	ca. 1,800	8,600
Pot residue.....	>307 (0.001)	-----	-----	2,950

Fraction 3 and the pot residue were useful media.

A center cut of Fraction 3 was taken and after suitable stripping and processing had a viscosity of 1888 cs. at 25° C. and $n_D^{25}=1.6183$.

There are provided, then, by the present invention media which because of their desirable viscosity, resistance to decomposition under electron bombardment, good resistivity, low vapor pressure and compatibility or nonreactivity with other elements of the projection system are admirably suited for the use described. It will be realized that obvious modifications of the invention may be made without departing from the spirit or scope thereof.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. In a projection system comprising a container having conducting interior, a deformable medium in said container, electron beam means for producing an electrical charge on the surface of said deformable medium as a function of an applied electrical signal and cooperating with said conducting interior to subject the medium to a deforming force to produce deformations in the surface of said medium and a light and optical system for projecting light as a function of the deformations in the surface of said medium, the improvement which comprises using as said deformable medium the Friedel-Crafts reaction product of benzyl chloride and a material selected from the class consisting of benzene, toluene, xylene, benzyl toluene, diphenyl methane, and mixtures thereof, said product having a viscosity of at least 100 centistokes (cs.) at 25° C.

2. In a projection system comprising a container having conducting interior, a deformable medium in said container, electron beam means for producing an electrical charge on the surface of said deformable medium as a function of an applied electrical signal and cooperating with said conducting interior to subject the medium to a deforming force to produce deformations in the surface of said medium and a light and optical system for projecting light as a function of the deformations in the surface of said medium, the improvement which comprises using as said deformable medium the Friedel-Crafts reaction product of benzyl chloride and benzene, said product having a viscosity of at least 100 centistokes (cs.) at 25° C.

3. In a projection system comprising a container having conducting interior, a deformable medium in said container, electron beam means for producing an electrical charge on the surface of said deformable medium as a function of an applied electrical signal and cooperating with said conducting interior to subject the medium to a deforming force to produce deformations in the surface of said medium and a light and optical system for projecting light as a function of the deformations in the surface of said medium, the improvement which comprises using as said deformable medium the Friedel-Crafts reaction product of benzyl chloride and toluene, said product having a viscosity of at least 100 centistokes (cs.) at 25° C.

4. In a projection system comprising a container having conducting interior, a deformable medium in said container, electron beam means for producing an electrical charge on the surface of said deformable medium as a function of an applied electrical signal and cooperating with said conducting interior to subject the medium to a deforming force to produce deformations in the surface of said medium and a light and optical system for projecting light as a function of the deformations in the surface of said medium, the improvement which comprises using as said deformable medium the Friedel-Crafts reaction product of benzyl chloride and xylene, said product having a viscosity of at least 100 centistokes (cs.) at 25° C.

5. In a projection system comprising a container having conducting interior, a deformable medium in said container, electron beam means for producing an electrical charge on the surface of said deformable medium as a function of an applied electrical signal and cooperating with said conducting interior to subject the medium to a deforming force to produce deformations in the surface of said medium and a light and optical system for projecting light as a function of the deformations in the surface of said medium, the improvement which comprises using as said deformable medium the Friedel-Crafts reaction product of benzyl chloride and benzyl toluene, said product having a viscosity of at least 100 centistokes (cs.) at 25° C.

6. In a projection system comprising a container having conducting interior, a deformable medium in said container, electron beam means for producing an electrical charge on the surface of said deformable medium as a function of an applied electrical signal and cooperating with said conducting interior to subject the medium to a deforming force to produce deformations in the surface of said medium and a light and optical system for projecting light as a function of the deformations in the surface of said medium, the improvement which comprises using as said deformable medium the Friedel-Crafts reaction product of benzyl chloride and diphenyl methane, said product having a viscosity of at least 100 centistokes (cs.) at 25° C.

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