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OPAQUE SHEETING AND METHOD OF MAKING SAME

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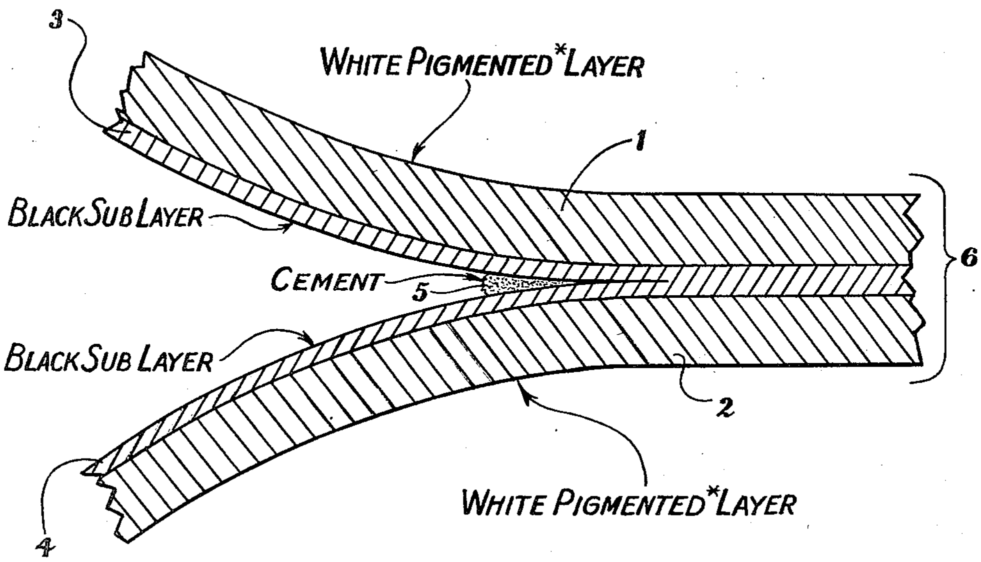

* LOW PIGMENT AND PLASTICIZER

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OPAQUE SHEETING AND METHOD OF MAKING SAME

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This invention relates to opaque sheeting and a process of producing such sheeting. More particularly this invention concerns an improved white plastic sheeting characterized by exceptional flexibility and thinness when considered with respect to the high opacity exhibited.

There are numerous instances in the art where there is a need for opaque sheets such as in the field of index cards, game cards and the like. For example, in the instance of index cards which are not sufficiently opaque, printed matter on the back or adjacent cards may show through, thereby causing reading difficulties or other confusion. In the instance of game cards, such as playing cards and the like which are held in the hands of players, it is apparent that opacity is a fundamental requirement in order that the characters on the cards will not show through and thereby be seen by opponents.

There are also various objects of art such as decorative items where it is desired that flexible opaque material may be available.

In the past, in order to produce opacity or density in such sheet material, it has been the practice to incorporate high amounts of heavy pigments and the like into the sheet stock for obtaining opacity. Titanium dioxide is an illustrative and frequently used pigment which has been incorporated to the extent of 15, 25 or 35 per cent into sheet stock for obtaining opacity of the sheet stock.

It is readily apparent that incorporation of high amounts of such pigment materials into the sheet stock for obtaining opacity degrades or otherwise weakens the physical properties of the sheet stock. The incorporation in large amounts of such components increases the weight of the stock as well as possibly the thickness, and is harmful to the flexibility of the sheet stock in that it causes it to become chalky. When such loaded sheet stock is subjected to severe bending a complete fracture may occur. Therefore, in attempting to obtain opacity by pigment incorporation, it has become necessary to compromise between loss in physical properties of the stock and the obtaining of a suitable density in the sheet material.

It is also disclosed in the prior art, in order to obtain a sheet stock which is relatively dense and through which light will not pass, to prepare a laminated sheet stock made up of three or more separate sheets. One combination comprises outer pigmented thin sheets having interposed therebetween a sheet-layer comprising some dense opaque sheet material. In some instances even thin metal foil sheets have been interposed in forming these three-sheet combinations, the metal foil inner sheet functioning to provide sufficient concentrated density that the resulting sheets are opaque. However, it is apparent that such sheets made up of three or more members necessarily become thick and bulky not only due to the plurality of sheets required, but due to the fact that there is involved at least two separate points of contact between the separate sheets which require adhesive lamination. Therefore, such composite sheets, while possessing some desirable properties relative to opacity, are prone

to be nonflexible, heavy, and stiff. Therefore such types of sheeting stock have not been satisfactory for purposes such as mentioned above where it is desired to have a relatively thin opaque and flexible sheeting stock.

After the investigation of numerous combinations I have found a relatively simple subbed sheeting laminate which not only is highly opaque, but exhibits unusual properties of flexibility and the like when considered in connection with the property of high density or opacity discussed above.

This invention has for one object to provide a sheeting stock which has particularly high opacity but yet is relatively thin and flexible. Still another object is to provide a white plastic sheet material which has a density in excess of 3, yet is relatively thick and flexible. A further object is to provide a highly opaque flexible sheeting stock of the class described which is particularly useful for business cards, game cards and the like purposes. Still a further object is to provide a relatively simple and economical method for manfacturing opaque, thin, flexible stock of the class described. Other objects will appear hereinafter.

For a further understanding of certain of the broader aspects of my invention, the following general description is set forth. I have found that thin sheet stock will tolerate a certain amount of pigment and plasticizer without unduly injuring the flexibility of the sheet or developing curl. However, such small amount of pigment incorporated in the sheet alone is insufficient to produce the desired opacity. That is, for example, it is possible to incorporate preferably not more than about 10% pigment such as titanium dioxide into a cellulosic thin sheet for securing some opacifying of the sheet without destroying thinness and flexibility of the sheet. However, the incorporation of this amount of pigment does not produce the necessary density for opacity. Stated in another way, the use of relatively small amounts of plasticizer should be emphasized in this structure, since by the laminar construction of this invention it is also possible to avoid using large amounts of plasticizer which are necessary if large amounts of pigments are used to maintain the physical properties of the sheet. In my structure the advantage of using small amounts of plasticizer is briefly: the production of a sheet having less tendency to curl or shrink since the loss of plasticizer by evaporation around the edges of the playing card would produce an effect known as "cupping."

To summarize: The use of a large amount of pigment, such as shown in the prior art structures, necessitates the use of large amounts of plasticizer to maintain flexibility. This dilution of the plastic reduces the tensile strength of the sheeting and its tear strength to a degree that makes it not useful for the purposes of my invention.

However, I have further found that a thin sheet, as just mentioned, pigmented with, for example, not more than about 10% of pigment (and preferably 8%) may have applied to one surface thereof a very thin coating of, for example, an ester of cellulose or the like containing dispersed carbon. This layer for convenience of description, is described as a carbon sub. Even though this coating is relatively thin, say of the order of $\frac{1}{10,000}$ inch in thickness, it imparts opacity to my thin sheet which has relatively low pigment and plasticizer therein.

An important step in the process of producing my sheeting stock is to laminate together two of such thin sheets as just described, the laminating being between the surfaces having the carbon sub. This laminating may be accomplished by the use of cement, solvent, heat and pressure. Likewise, the subbing of the sheets may be in accordance with conventional coating procedure and in a continuous manner.

In order to provide a still further understanding of my invention, reference may be made to the attached drawing forming a part of the present application. The drawing comprises a semidiagrammatic side elevation view on a very much enlarged scale illustrating the crosssectional construction of my new opaque sheeting stock. Referring to this drawing my sheeting stock is made up of low pigmented and plasticized base materials **1** and **2** of an identical or substantially identical nature. These base materials are coated with a black "sub" as indicated at **3** and **4**. The two sheets thus coated are, in any conventional manner, cemented or otherwise laminated together by the incorporation of a small amount of cement at the interface between the "sub" surfaces of the two base sheets, namely, the incorporation of cement as indicated at **5**. This results in a relatively flexible opaque sheet stock as indicated overall at **6**, which sheet stock is comprised of two "subbed" separate sheets **1** and **2** as already mentioned, as contrasted to prior constructions utilizing three or more sheets.

In further regard to the continuous production of my new sheeting stock, the following general considerations apply. The thin base stock containing not more than 8 or 10% pigment and preferably corresponding low plasticizer is either made up in the conventional manner or procured commercially in the open market. Such thin base stock is usually comprised of a cellulose ester such as cellulose acetate or cellulose acetate butyrate containing one or more plasticizers exemplified by triphenyl phosphate and the various phthalates such as methoxyethyl phthalate, ethyl phthalate, butyl phthalate, and the like. As already indicated, this base stock has been pigmented in the usual manner such as by mixing titanium dioxide not in excess of 10% with the dope from which the sheet is formed. A roll of this sheeting is unwound in a usual manner with respect to a subbing roll, hopper, or the like, from which there is continuously applied a very minute coating of a cellulose ester having dispersed therein carbon particles. This subbing layer may be applied from a solvent solution made up of a ketone solvent, halogenated hydrocarbon solvents, alcohol and the like, the solvent softening the surface of the pigmented base sheet in a manner that the carbon particle cellulose layer becomes firmly bonded to the surface being coated. In certain instances, as will be apparent from the examples, aqueous emulsions may be used.

In a similar manner, another roll of base sheeting may be continuously coated with a carbon sub in accordance with the procedure exactly the same as that just set forth.

The two sheets thus formed, each having a carbon sub on one surface, are then brought between pressure rolls in such a manner that the carbon subbed surface of one sheet may be laminated continuously to the carbon subbed surface of the other sheet. This lamination may be accomplished by using a cementing solution in the conventional manner, to produce a strong bond.

By the use of the above technique, it is possible to obtain sheets, for example 0.01 of an inch thick and which have only 0.1% light transmission. In addition to such sheets being relatively thin, they are very flexible and withstand repeated bending and folding. As discussed above, products of the prior art if made of like thinness would have a light transmission of greater than 1%. On the other hand, if prior art products were made to have a lower light transmission such products would be much thicker and/or brittle, because of the heavy incorporation of pigment and otherwise would be disadvantageous.

A still further understanding of my invention will be had from a consideration of the following specific examples.

Example 1

In connection with this example, the base stock was comprised of thin cellulose acetate sheeting commercially obtainable prepared from cellulose acetate having 38 to 43½% acetyl radical. This cellulose acetate sheeting was about .005 inch in thickness and was plasticized with about 10% triphenyl phosphate plasticizer. The base sheet contained 5% titanium dioxide pigment and therefore transmitted some light. This thin base sheeting was subbed on one side with a sub comprising a solution of 3% cellulose nitrate and 0.8% carbon black in a solvent composed of 75% acetone and 25% methyl alcohol.

The carbon black used in this particular example was a commercial carbon black known as Peerless lamp black. The thickness of this carbon black sub applied was of the order of about .0001 inch. Then the sheets thus subbed were laminated together using a cement comprised of 5% cellulose nitrate dissolved in 75% acetone and 25% methyl alcohol.

The lamination was accomplished by passing the sheets, having their surfaces wet with cement, through pressure rolls operating at about 40 lbs. pressure, per square inch. The result was a white laminated sheet which was of a total thickness of about 0.01 of an inch and exhibited a density of greater than 3.5. Also this sheet had fold and tear properties 50% greater than a white sheeting stock which possessed a density only of the order of 2.5

Example 2

In connection with this example, the base used was comprised of cellulose acetate butyrate of the following composition and thickness:

Acetyl content	per cent	30
Butyryl content	do	17
Thickness	inches	.005

Likewise, this is a commercially available thin sheeting. The sheeting contained approximately 8% titanium dioxide pigment to provide a white sheeting and was likewise plasticized with about 8% triphenyl phosphate. The thin base sheeting was subbed with a carbon black, dispersed in a solvent mixture of 3 parts acetone and 1 part methyl alcohol in a manner described similar to that of Example 1. Thereafter the resultant subbed sheets are laminated together using a cement and passed through pressure rolls. The resultant white sheeting stock possessed a density in excess of 3.8 and was very flexible and tear resistant. The "flexibility" and "tear" were measured in the manner referred to hereinafter; namely, by a standard research tear tester as shown in T. A. P. P. I. Standard T414-40 and in a Shopper fold tester according to A. S. T. M. Standard No. D643-43, Method A.

Example 3

In accordance with this example, the cellulose acetate butyrate sheeting as in Example 2 was employed except that the sheeting was plasticized with 5% butyl phthalate plasticizer. The sheeting had only about 8% titanium dioxide pigment therein. The sheeting was subbed with a carbon black layer and laminated as in Example 1. The carbon black solution was comprised of 3% cellulose acetate and 1.0% carbon black dissolved in a mixture of 3 parts ethylene chloride and 1 part methyl alcohol. The cement solution was comprised of 3% cellulose acetate in methyl phthalate.

Example 4

In this example the thin base stock was comprised of a commercially available vinyl chloride-vinyl acetate copolymer sheet. This thin sheet was composed of approximately 80% vinyl chloride and 20% vinyl acetate. The sheet material was .005" thick and contained 10% titanium dioxide pigment. One surface of the sheet was subbed in accordance with the present invention with a carbon black containing solution by a procedure similar to the procedure already described above in Example 1.

Two sheets of the black coated vinyl stock prepared as aforementioned were joined (black to black) by passage through pressure rolls operated at 150° F. and approximately 100# per square inch pressure. It is to be observed that this particular example accomplishes the lamination by means of heated pressure rolls. There resulted a white flexible sheet of .010" thickness, which sheet exhibited a density in excess of 3.

Further appreciation of the merits of my invention may be had from consideration of the data in the following table. In this table, samples 1 to 6 concern prior art type of sheeting wherein the pigment content has been substantially increased up to 40% for the purpose of obtaining opacity. It will be observed from sample 6 that while the density increases somewhat, by increasing the pigment content, the fold property drops off to 0.

Samples 7, 8 and 9 are also illustrations of prior art materials, but in which a mixed ester sheeting has been employed.

Samples 10 and 11 as further noted by the designations (B) and (C) are illustrative samples of sheeting in accordance with the present invention. It will be observed that the density of the sheets in accordance with the present invention is substantially in excess of any density in samples 1 to 9. In addition, the fold and tear properties of samples 10 and 11 in accordance with the present invention are superior to that obtainable in any of the samples 1 to 9 aforementioned.

TABLE

Sample Number	Cellulose Acetate		Folds	Tear	Density
	Percent TiO_2	Plasticizer			
1	8	15% triphenyl phosphate; 15% methoxyethyl phthalate	2	118	1.60
2	15	15% triphenyl phosphate; 15% methoxyethyl phthalate	3	86	2.4
3	18	14% triphenyl phosphate; 14% methoxyethyl phthalate	3	163	2.8
4	20	15% triphenyl phosphate; 15% methoxyethyl phthalate	4	85	1.82
5	25	15% triphenyl phosphate; 15% methoxyethyl phthalate	4	100	3.05
6	40	15% triphenyl phosphate; 15% methoxyethyl phthalate	0	70	2.48
	Cellulose Acetate Butyrate—17% Butyrate				
7	8	8% triphenyl phosphate	4	135	1.74
8	20	do	2	110	1.92
9	40	do	0	(A)	2.30
10	8(B)	do	7	121	3.90
11	8(C)	do	8	115	3.85

(A) Tear could not be measured.
(B) Black interlayer as described in present invention. (Roll #87-25/1546)
(C) Black interlayer as described in present invention. (Roll #87/3926)

In the above table the density was measured by a Densichron as outlined in The Review of Scientific Instruments, pages 79–82, volume 19, February 1948.

The tear was measured by a standard Research Tear tester in the manner as shown in T. A. P. P. I. Standard T414–40.

The fold was measured by the Shopper fold tester according to A. S. T. M. Standard #D643–43 Method A.

It may be seen from the above examples that I have provided as new opaque thin sheet stock which is useful for business index cards, game cards, decorative objects and the like where opacity is a required or desirable property. In addition to my new sheet stock being relatively thin, it exhibits excellent properties from the fold and tear standpoint. My new sheet stock is relatively thin in that it comprises only two sheets of relatively low pigmented base material as contrasted to the prior art use of 3 or more sheets or the inclusion of very high amounts of pigment for obtaining opacity.

As pointed out above, my new sheet stock is preferably made up of two base sheets from cellulose organic esters plasticized by triphenyl phosphate, but other various plasticizers may be employed. It is essential, however, as emphasized above that the pigment content of my base sheet be maintained preferably below 10% and around 8% for titanium dioxide is quite satisfactory. In partial or complete replacement of titanium dioxide for pigment, other pigments such as zinc oxide may be used. Rather than make a pure white sheet stock, it is possible to incorporate pigments having a slight color such as chrome green, etc. or TiO_2 and Prussion Blue to obtain various pastel shades. While in several of the foregoing examples I have referred to applying a carbon black sub carried in a cellulose nitrate environment and in a ketone and alcohol solvent, it is also possible to employ the sub in a cellulose acetate or cellulose acetate butyrate environment together with appropriate solvents. In some instance aqueous emulsions may be advantageous. While the examples in this application have shown the use of a pigment in the amounts of either 5% or 8%, it is possible generally to use such a pigment in the amount ranging from 5% to 10% or even more where the physical properties of the sheet are not deteriorated by such addition. I have also referred to the use of 8 to 10% plasticizer in my examples. The amount of plasticizer used will vary depending on the type of cellulose ester or other plastic used. For example, cellulose acetate may advantageously use somewhat more plasticizer than a cellulose acetate butyrate to preserve the flexibility required. In general, the range of plasticizer used in this invention will be only that necessary to plasticize the ester or other plastic used; excessive amounts will not be required to preserve flexibility lost by the addition of excessive amounts of pigment as in the prior art. Certain other changes and advantages will be apparent from the foregoing description.

I claim:

1. The process of producing an opaque sheet stock characterized by its high density and excellent fold and tear resistance which comprises coating one side of a thin sheet with a coating solution containing carbon black whereby the opacity of the sheet is increased, the thin sheet being characterized in that it contains not more than 10% pigment, laminating two of the aforementioned coated sheets together, the lamination being between the surfaces having the carbon surfacing layer, accomplishing the lamination by means of cementing, heat and pressure whereby a finished sheeting stock is obtained having excellent fold and tear resistance and having a density in excess of 3 as measured by a "Densichron."

2. The process of producing a white opaque sheet stock characterized by its high density and excellent fold and tear resistance which comprises coating one side of a thin white plastic sheeting with a coating solution containing carbon black the thin white sheeting being characterized in that its thickness is no greater than $\frac{5}{1000}$ of an inch and contains not more than 10% white pigment, laminating two of the aforementioned coated thin sheets together, the lamination being between the surfaces carrying the carbon surfacing layer whereby a finished sheeting stock is obtained having excellent fold and tear resistance and having a density in excess of 3 as measured by a "Densichron."

3. The process of producing an opaque sheet stock characterized by its high density and excellent fold and tear resistance which comprises coating one side of a sheet with a coating solution containing an opacifying agent, the sheet being characterized in that it contains not more than 10% pigment, laminating two of the aforementioned sheets together, the lamination being between the surfaces having the coated layer whereby a finished sheeting stock is obtained having excellent fold and tear resistance and having a density in excess of 3 as measured by a "Densichron."

4. The process of producing an opaque cellulose ester sheet stock characterized by its high density and excellent fold and tear resistance, which comprises coating a side of a thin sheet with a coating solution containing carbon black, whereby the opacity of the sheet is increased, the sheet being characterized in that it consists essentially of cellulose ester, said cellulose ester containing both plasticizer and pigment, but the amount of each thereof not exceeding 10%, laminating two of the aforementioned coated sheets together, the lamination being between the surfaces having the carbon surfacing layer, accomplishing the lamination by means of cementing

heat and pressure, whereby a finished sheeting stock is obtained having excellent fold and tear resistance.

5. A highly opaque laminated sheet stock characterized by its relative thinness and excellent fold and tear resistance, said stock being essentially comprised of two sheets of a thin sheeting made up of material selected from the group consisting of cellulose acetate and cellulose acetate butyrate, said sheets containing from 5% to not more than 10% pigment and plasticized with 8–10% of a plasticizer selected from the group consisting of phosphates and phthalates, the sheets carrying a carbon black containing surfacing layer, said laminated structure comprising the bonded surfaces of the sheets carrying such carbon black layer, the bonding being at the interface of said layers, whereby the aforementioned highly opaque sheet stock is obtained having high flexibility and tear resistance.

6. A highly opaque laminated sheet stock characterized by its relative thinness and excellent fold and tear resistance, said stock being essentially comprised of two plastic sheets containing from 5% to not more than 10% pigment, the sheets carrying a carbon black surfacing layer, said laminated structure comprising the bonded surfaces of the sheets carrying such carbon black layer, the bonding being at the interface of said layers, whereby the aforementioned highly opaque sheet stock is obtained.

7. A highly opaque laminated sheet stock characterized by its relative thinness and excellent fold and tear resistance, said stock being essentially comprised of two sheets of a thin sheeting material of cellulose acetate, said sheets containing some pigment but not more than 10% pigment, the two cellulose acetate sheets carrying a carbon black surfacing layer, said laminated structure comprising the bonded surfaces of the sheets carrying the carbon black layer, the bonding being at the interface of said layers, whereby the aforementioned highly opaque sheet stock is obtained.

8. An opaque sheeting stock characterized by exhibiting a density in excess of 3 as measured by a "Densichron," fold properties in excess of 5, as measured by a "Shopper" fold tester according to A. S. T. M. Standard #D643–43 Method A, and tear properties in excess of 100 as measured by the method of T. A. P. P. I. Standard T414–40, said stock being comprised of pigmented outer plastic cellulose ester sheet surfaces, the pigment contained in said sheet stock being between 5 and 10%, the outer sheets having interposed therebetween a thin interlayer containing carbon particles, the outer surfaces and the interlayers being securely bound together.

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