The present invention relates to transparent films formed of a thermoplastic material such as a cellulose derivative or an artificial resin.

The invention particularly relates to such films which are intended for use under circumstances in which they have to withstand considerable wear, such as, for example, films for use as the surface layers of sound records which are adapted to actuate a reproducing stylus.

It is known to make pictorial sound records by pressing transparent films of cellulose material onto a paper base which is printed with pictorial, advertising or descriptive matter.

The clear cellulose material forming the playing surface of such records, however, is easily torn up by the sharp point of an ordinary steel needle, and these records can only be played satisfactorily if a run-in needle is used, i.e., one which has had the sharp edge removed by playing on a record made with shellac or other hard substance as a base. Furthermore, the soft nature of the material gives rise to a high degree of friction at the point of the needle, and in many cases, the records cannot be played on a portable talking machine or any talking machine where an ample reserve of driving power is not available.

It is well known that resistance to the tearing action of the needle point may be obtained by introducing mineral fillers into the material, but hitherto, this has not been possible in the case of pictorial records of the type in question because of the necessity for maintaining transparency in the surface layer. We have now discovered that certain forms of naturally occurring silica can be introduced into plastic cellulose compositions to give resistance to the tearing action of the needle, without destroying the transparency of the material when in a thin layer, as for instance in thickness of 0.005" to 0.010", which are suitable thicknesses for the playing surfaces of records of the type referred to.

We refer particularly to that form of absorptive silica known as diatomaceous earth, deposits of which occur in almost every country in the world, and which comprise the fossilized remains of microscopic plants or diatoms. It is of great importance that the diatomaceous earth used should be light in color and as free as possible from impurities such as oxides of iron and aluminum, clay, sand, chalk and magnesia. All of these impurities will detract from the transparency of the film. It is also equally important that the earth should be as fine as possible. We have found that when the filler particles do not exceed 0.010 millimetre in diameter, it is possible to introduce as much as 30 per cent of it into the cellulose composition without serious loss of transparency in a film 0.005" to 0.010" in thickness. 5 per cent of diatomaceous earth of the requisite degree of fineness contained in a cellulose acetate film 0.020" in thickness was practically invisible. When the size of the filler particles exceeds 0.020 mm. in diameter, the film is rendered opaque. Particle sizes of 0.010 mm. and 0.020 mm. diameter correspond to sieve meshes of approximately 1200 and 600 respectively. It may be said that the most desirable varieties of diatomaceous earth are those having a high silica content together with a high absorbptivity, and which will pass completely through a hypothetical 1000 mesh sieve.

It should be understood that under the term "cellulose compositions", we include organic and inorganic esters of cellulose, examples of which are acetyl cellulose and nitro-cellulose, respectively, and also cellulose ethers, such as, for example, benzyl cellulose and ethyl cellulose.

The cellulose compositions may be prepared by any known processes and may involve the use of volatile solvents such as acetone, dimethyl ketone, alcohol, benzene or the like. They may also contain high boiling solvents, or plastifier such as camphor, or camphor substitutes, as, for example, triphenyl phosphate, diethyl phthalate, tricacetin, alkylated sulphoxamide derivatives of aromatic hydrocarbons, or the like. The manufacture of the material may be carried out by the known processes of masticating, mixing, or kneading with volatile solvents to form a dope or varnish, or a material of a putty-like consistency which may be spread onto the printed paper and dried, or, alternatively, may be spread onto a non-adherent surface, dried, and stripped as a film.

The materials may also be worked together with limited quantities of volatile solvents to form a horny mass which may be further mixed on rollers, pressed into blocks and sliced into sheets of the desired thickness. By other known methods, the surface films may be prepared according to processes of working the materials together on heated rolls with, or without volatile solvents, plastifying agents, etc., to form a rubbery mass which is then passed between heavy calender rolls to form a thin sheet.

We have also discovered that diatomaceous earth of the type described may be incorporated with various synthetic resins which are colorless or only lightly colored. The same result in re-
gard to transparency is obtained as with the cellulose compositions. For example, a urea-thio-
urea-formaldehyde resinous condensation product containing a flexibilizer such as glycercine or
a glycercy derivative may be loaded with 30 per-
cent of diatomaceous earth and worked up into a thin film which is transparent. Other suitable
colorless synthetic resins of known type are pre-
pared from glycercine and phthalic anhydride, vinyl acetate and vinyl chloride. Mixtures of the
above with cellulose compositions may also be
employed.
Thus, according to the present invention, a
transparent film or layer having as basis a ma-
terial such as a cellulose derivative or a synthetic
resin contains a filler consisting of a naturally
occurring silica such as diatomaceous earth.
By way of example, two processes for the pre-
paration of transparent films for sound records
will now be described.
Process I.—40 parts of powdered, low viscosity
cellosolve acetate, preferably of 40 mesh fineness,
are mixed with 30 parts of finely divided (1,000
mesh) diatomaceous earth, together with 4% parts of triphenyl phosphate, 12% parts of diethyl
phthalate and 1½ parts of toluene sulphonamide.
It should be understood that any other
known plasticizers for cellulose acetate may be used
providing they are capable of yielding light-
colored acetate films.
The selection of plasticizer is not vital to the
transparency of the film, but it is obviously ad-
vantagous to avoid those plasticizers known to
produce dark colored products inssofar as a dark
transparent film will not give the same true value
to the printed colors as a colorless film.
The mixed materials are heated and mixed either
in a masticating machine or on rollers, preferably in the presence of a small quantity of
acetic acid or other volatile solvent until a plastic
mass is produced which is completely free from
white specks of cellulose acetate. The presence
of a small amount of solvent enables plastifica-
tion to be carried out at a relatively low tempera-
ture such as 100° F. During the process of mixing
on the rolls, the solvent is slowly volatilized,
the plastic mass gradually becoming stiffer.
At a suitable stage of the process, the plastic
material is withdrawn from the mixer and passed
between heavy calender rolls to form thin sheets
of from 0.005" to 0.010" in thickness.
The sheets are hung for several days in a heated
ed, ventilated chamber at a temperature of approx-
imately 100° F. for the purpose of eliminat-
ing the last traces of solvent. Discs of suitable
diameter (which may appear translucent at this
stage) are cut from the sheets and are then ready
for combining with the printed paper core layer
to form the completed record.
Either a single thickness of paper printed on
each side may be used or, if more convenient, two
down, each printed on one side, may be
joined on their unprinted sides by means of a
thin layer of shellac or other adhesive, or the
record can be built up by the use of a plurality of
cemented layers of paper to any desired thick-
ness.
The layers are assembled between steam-heated
matrices or pressing plates in a hydraulic press,
the transparent film being, of course, immediate-
ly adjacent to the heated plates. Pressure is ap-
plied, the layers are amalgamated, and the sound
impression is formed. Finally, the record is
cooled before releasing the pressure.
During the pressing process, the surface films
are rendered more transparent and become more
flexible. The printed design on the paper be-
neath the surface then stands out clearly.
Instead of low viscosity cellulose acetate, me-
dium or high viscosity cellulose acetates may be
used, or benzyl cellulose or any other suitable cel-
 lulose derivative.
Process II.—A resin syrup is first prepared by
condensing in known manner urea or thiourea
with formaldehyde, the water content of the syrup
being subsequently reduced to approximately 10
per cent by evaporation. Mixtures of urea and
thiourea may also be employed. The viscous
syrup is then run into this form as a base for the
surface composition, and in accordance with the
invention may be incorporated with diatomaceous
earth and flexibilized in the following propor-
tions:

<table>
<thead>
<tr>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea or thiourea resin syrup (10% water)</td>
</tr>
</tbody>
</table>
| Diethylene glycol (or other glyceryl der-
ivative) | 25 |
| Diatomaceous earth | 25 |

A small amount of oxalic acid (for example
1% to 3%, reckoned on the resin content) may be
added to accelerate the subsequent hardening
of the surface film during the pressing operation.
If preferred, other organic acids, such, for ex-
ample, as salicylic acid, tartaric acid, or citric
acid may be employed as accelerators.
The filling agent is milled with the mixture of
ethylen glycol and resin syrup, alcohol being added at discretion to produce a consistency suit-
able for spreading. A dry coating of suitable
thickness is obtained by applying to the printed
design or varnish coat .010"-.015" in
thickness, or, preferably, by applying the suc-
cession of thinner coats, until the desired thickness
is reached. After having been coated, the var-
ished printed paper discs or sheets are dried for
1 hour at 65° C. and finally impregnated with the
sound grooves by pressing between heated
matrices at a temperature of 280°-310° F. It has
been found that a complete cure of the resin com-
position is effected in 15-30 seconds when a pres-
sure of approximately 1500 lbs. per square inch
and a temperature of 300° F. are employed.
In either of the two processes described above,
if it is desired to enclose completely or to seal
the edges of the paper discs, the latter should be
made smaller in diameter than the surfaces, as for
example 9½" for a record having a finished over-
al diameter of 9½", so that the two overlapping
clear films will be joined together at the edge by
the pressure of the rings holding the matrices.
In the foregoing examples, the invention has
been described as adapted specifically to the
production of transparent films for sound rec-
ords, but it will be clear that such films will find
application as surface coatings in a variety of cir-
cumstances in which resistance to wear is an es-
tential property of the coating.
Many modifications of the processes hereinbe-
fore described will be apparent to one skilled in
the art, and it is to be understood that the inven-
tion is not to be limited to the particular ex-
amples given but only insofar as it is defined by
the appended claims.
We claim as our invention
1. A composition of matter comprising a
thermoplastic material which is transparent in
thin sheet form and which has incorporated therein a filler of diatomaceous earth substantially free from coloring oxides, said filler being of a particle size insufficient to substantially alter the transparency thereof and in an amount sufficient to impart wear resistance to said material under the action of a phonograph needle.

2. A composition of matter according to claim 1 wherein the thermoplastic material comprises a cellulose derivative and wherein the weight of the filler is substantially three-quarters that of the cellulose derivative.

3. A composition of matter according to claim 1 wherein the thermoplastic material comprises a synthetic resin and wherein the weight of the filler is substantially one-half that of the resin.

4. The method of forming phonograph records which comprises mixing with a material adapted to have sound grooves formed therein and which is transparent when in thin sheet form diatomaceous earth substantially free from coloring oxides and reduced to a particle size such that no loss of transparency in said material will result therefrom, the diatomaceous earth being in an amount sufficient to impart wear resistance to the record.

5. The method of forming phonograph records which comprises mixing with a reactive synthetic resin which cures to transparent form in thin sheets and which is adapted to have sound grooves formed therein, a filler of diatomaceous earth substantially free from coloring oxides and reduced to a particle size such that no loss of transparency in said resin will result therefrom, the diatomaceous earth being in an amount sufficient to impart wear resistance to the record.

6. The invention set forth in claim 5 characterized in that the indices of refraction of the diatomaceous earth and the cured resin are substantially the same.

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