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POLYSTYRENE PHONOGRAPH RECORD COMPOSITION AND METHOD OF MAKING SAME

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This invention relates to polystyrene phonograph records, compositions for producing such records, and processes for producing the records and compositions, particularly compositions for and processes of producing the so-called "33⅓" R. P. M. and "45" R. P. M. records by injection molding.

A few years ago, the majority of disc records were relatively heavy and thick, played at a standard speed of 78 revolutions per minute and carried from about 96 to 120 recording grooves per inch of diameter. Then came the demand for a longer playing record and the answer was records which play at 33⅓ or 45 R. P. M. (the "long play" or "L. P." records) and carry from about 200 to 300 grooves per inch.

The present invention is concerned principally with the production of "33⅓" and "45" records which are light weight, thin, strong, long wearing, have high fidelity and low background noise, and are low in manufacturing cost.

The grooves in a record are in the general shape of a V and the undulations which cause sound are in the walls of the V so that the needle of the playing instrument moves more or less horizontally. It will be obvious that the greater the number of grooves per inch, the smaller, narrower, shallower and closer the grooves must be, the greater is the danger that the walls of adjacent grooves will break or wear into each other and that the lands between the grooves will be so thin that there is danger of the needle jumping from one micro groove to the next.

The material with which the present invention is concerned is moldable by injection molding giving low manufacturing costs, it completely fills the record mold and faithfully reproduces even the most minute depressions and ridges of the mold face, yet the molded record plays well on the first play and for more than the usual number of subsequent plays (100 plays is the usual test for a 10 in. 33⅓ R. P. M. record) with substantially no background noise and no deterioration or increase in background noise. The same material may be used for molding "78" records and may also be used for molding any type of record by compression methods.

In accordance with one aspect of the invention, polystyrene sound record compounds of improved wear resistance and low background noise are obtained by the use of a special silicon carbide-polystyrene resin master-batch which is prepared by initially grinding the silicon carbide in a small amount of polystyrene until the sharp edges of the carbide particles are ground off and the particles are thoroughly wetted with the resin, for instance for a period of one hour on a 2-roll mill, and then using this material to give a controlled abrasive action of the final record molding material on the playing stylus. Although developed primarily for use in microgroove record compounds, the use of these special master-batches of silicon carbide in regular groove (78 R. P. M.) compounds results in records of improved quality.

Using the special silicon carbide mix, compounds containing from 0.01 part to 0.035 part, by weight, of silicon carbide from which microgroove records may be injection molded, give records having improved sound and wear characteristics and also produce a minimum of wear on the needles used to play them. Larger amounts of silicon carbide, although enhancing the wear resistance of the record, cause excessive needle wear.

The silicon carbide used in the special polystyrene master-batch has, as purchased, irregular sharp-edged particles ranging in size from 0.1 micron to approximately 10 microns (average 5–6 microns) as determined by electronmicroscope photographs. Crystalon 4FX and Carborundum FFFFRA, proprietary brands of silicon carbide, as well as other brands of silicon carbide or boron carbide, which may replace silicon carbide, having similar characteristics may be used.

It is found that when a filler such as silicon carbide is processed with a small amount of polystyrene on a two roll mill for a period of about one hour, the sharp edges of the particles are ground down and the particle size to some extent reduced. In addition, this operation wets the carbide particles with polystyrene thus making for easier dispersion in the final compounding operation and a better bonding of the particles to the polystyrene. The use of the specially prepared master-batch enables control of the action of the carbide on the needle wear to be maintained and makes it possible to obtain a balance between needle wear and the wear resistance of the record.

All of these factors influence the production of sound records of improved wear quality. Microgroove records, both 33⅓ and 45 R. P. M., prepared from either compression molding or injection molding compounds containing the special carbide master-batches are free from harshness or ticks which are occasionally present in records prepared with virgin filler. In addition to the controlled wear of the carbide on the needle, the presence of this material dispersed throughout the record material seems to minimize the action of the needle on the composition and this is accomplished without a dusting of the record surface.

The special processing technique used for the production of the silicon carbide master-batch is to first prepare a blend containing approximately 50 parts by weight of the polystyrene resin with 50 parts by weight of the silicon carbide. Also in this batch is preferably a small quantity of an antioxidant, for instance 2,6 ditertiary butyl para cresol, marketed under the proprietary mark Ionol, to reduce the molecular weight degradation of the resin during processing. In addition, a very small quantity of zinc stearate is preferably added to facilitate release of the compound from the rolls of the mill. These materials are then processed on a 2-roll mill having roll surface temperatures of 160–165° C., for one hour after the materials are fluxed. During this period, the silicon carbide particles are ground and constantly worked so that the sharp edges are removed. After the mix is completely compounded on the roll mill the master-batch thus prepared is sheeted off and granulated.

Using this special carbide master batch, record compounds containing from 0.01 part to 0.035 part by weight of silicon carbide may be prepared from which microgroove records may be molded having improved sound and wear characteristics and with commercially satisfactory needle wear on all types of needles. The use of larger amounts of silicon carbide gives records of good wear resistance but needle wear is excessive. Records produced from compounds containing as low as 0.01 part of silicon carbide which has not been specially processed are of inferior quality in that the surface becomes dusted after long playing and the sound quality is inferior. By using the master-batch, a balance between wear resistance and needle wear may be obtained and records may be

produced giving a minimum of needle wear but yet having good wear resistance.

To facilitate and complete dispersion of the master batch in the finished compounds, the special silicon carbide resin master-batch is preferably further processed with additional resin and zinc stearate through a Banbury and 2-roll mill to make a polystyrene silicon carbide mix containing a definite amount of the carbide, for instance 3.5 percent. This material after sheeting from the roll mill is granulated and a small amount is used in the finished compound. The dilution of the master-batch tends to ensure uniform distribution of the carbide particles in the final molding composition.

Example 1

A typical formulation for a black record injection molding material is

	Parts by weight
Polystyrene	100
Carnauba wax No. 1 yellow	3
Microcrystalline wax (crown wax 1035)	3
Zinc stearate	1
Wetting - emulsifying - surface active agent (Anatrox D-100)	0.25
Carbon black (Kosmos BB)	2.00
Silicon carbide (processed as described)	0.01–0.035

In order to produce a good record, it is necessary to have all of these materials in a homogeneous mixture and to have the unmeltable solids firmly bound in place; and it is also necessary that the walls of the grooves upon which the needle bears be as firm and smooth as possible.

To obtain a good final record molding material the master batch system is used. A typical master batch composition may be made in the following manner.

Materials:	Parts by weight
Carborundum FFFFRA	2.0
Polystyrene resin	1.99
Ionol	0.002
Zinc stearate	0.01

The Ionol, antioxidant, was added to avoid excessive degradation of the resin. The zinc stearate acts as a lubricant to facilitate the removal of the materials from the roll mill after processing. Instead of the Ionol, one may use diphenylparaphenylenediamine or a mixture of mono and di-heptyldiphenylamine or other suitable antioxidants. Instead of the zinc stearate one may use calcium, magnesium, barium, lead or manganese stearates.

The polystyrene resin referred to herein has an average relative molecular weight of from 50,000 to 150,000 with a preferred range from 55,000 to 70,000 and a Rossi-Peakes flow of 60 to 1000 seconds with a preferred range of 60 to 300 seconds. The Rossi-Peakes flow test is described in an article "Measuring the Plasticity of Hot Molding Compounds" by Gilbert L. Peakes, published in "Plastic Products," February, March, and April issues, 1934. The flow values given were determined by ASTM test No. D569–48 modified in that the test specimens were prepared in tablet form from 0.52 gram weights of material, the working pressure was 1000 pounds per square inch, the temperature was 135+0.1° C. and the flow was measured for 1.5 inches. The molecular weight is determined by dilute solution viscosity methods according to the following formula

$$\text{Relative viscosity} = \frac{\text{time for solution to discharge from pipette}}{\text{time for solvent to discharge from pipette}}$$

using a solution containing 0.1000 gram of polymer per 100 milliliters of benzene free from thiophene, measurements being made at 20° C.

Specific viscosity = relative viscosity −1

$$\text{Molecular weight} = \frac{(57{,}800)(\text{specific viscosity})}{C}$$

C=0.1000 gm. per 100 ml.

The polystyrene, silicon carbide, zinc stearate and antioxidant were first preblended in a mixer and then transferred to the 2-roll mill with roll surface temperatures of 160–165° C. The mixture was processed on the roll mill to ensure continuous working of the silicon carbide and complete grinding of the particles. In lots of 40 pounds on a 36 inch mill with rolls 16 inches in diameter, the processing was complete in about 60 minutes but more or less time may be consumed, the idea being to mill until very thoroughly compounded and the edges of the particles dulled, as indicated in tests on sample records, which can be accomplished under the above conditions.

The above master-batch was then further processed by compounding with more polystyrene in a Banbury or on the roll mill with roll surface temperatures of 160–165° C., the proportions of materials being

Materials:	Parts by weight
Master batch	28.00
Polystyrene resin	370.00
Zinc stearate	2.00

This gave the basic polystyrene-silicon carbide mix containing principally 14 parts of silicon carbide in 384 parts of resin. The zinc stearate prevents sticking in the machines. If the mix is thoroughly pre-mixed or pre-blended in a Banbury prior to transfer to the roll mill, the milling may take only 15 minutes after the materials are fluxed, the idea of this step being to have the silicon carbide thoroughly dispersed throughout the resin. After milling, the mix is preferably granulated for convenience in weighing. The steps of making the master batch and the basic polystyrene-silicon carbide mix may be combined if desired but grinding the rough and sharp edges off the silicon carbide particles usually occurs in less time the smaller the amount of resin, the amount of resin being sufficient to hold the particles and let them grind against one another and against the surfaces of the rolls yet prevent the particles from bearing against one another or the rolls with so much force that the sharp edge are broken off and other sharp edges formed rather than ground off; too great dispersion of the particles results in relatively few of the particles contacting each other or the roll surfaces in a given time and gives inefficient grinding of the sharp edges of the particles. Mixing virgin carbide into the polystyrene in the proportions in which they appear in the finished record compound and milling such a composition gives no dulling of the carbide particles. The object in making the basic polystyrene-silicon carbide mix is to distribute the carbide particles in a relatively large mass of resin because, in the step next to be described, such a minute quantity of the particles is to be used that it is more efficient to distribute them from a dilute dispersion than endeavor to distribute them from a more concentrated dispersion. If desired, more or less polystyrene than the 370 parts previously given may be used but the amount given combines efficient mixing in diluting the master-batch with efficient distribution of particles in the final molding material without involving double processing of larger amounts of material.

In the record molding material of the following formula

Material:	Parts by weight
Polystyrene	100.00
Carnauba wax	3.00
Crown wax 1035	3.00
Zinc stearate	1.00
Antarox D–100	0.25
Carbon black (Kosmos BB)	2.00
Silicon carbide (processed)	0.01

The silicon carbide is from the master-batch, sufficient of the basic polystyrene-silicon carbide mix being used to give the stated amount of carbide. The amount of polystyrene includes the amount added with the carbide

particles and allowance should be made for the polystyrene added in this manner. In case the amount of silicon carbide used is 0.035 part, proportionately more polystyrene must be allowed for. The antioxidant originally used in the mast-batch is so attenuated in the molding material that it is not shown in the above formula. The carnauba wax may be substituted in whole or in part by microcrystalline saponifiable waxes modified to have melting points of 180–185° F., acid numbers of 20–25 and saponification numbers of 55;65. Crown waxes Nos. 23 and 36 and vegetable waxes such as candelilla wax meet these specifications and may replace carnauba wax.

The crown wax 1035 is a microcrystalline petroleum branched chain paraffin of from 50 to 65 carbon atoms. It has a melting point between 91° and 93° C. The acid number, saponification number and iodine value are nil. Other waxes having similar properties may be substituted for crown wax 1035.

The Antarox D–100 is a polyethylene glycol oleyl ether. It is a gel with a melting point of 43° C.; stable to acids, alkali, hard water, boiling water, metal ions and on storage; soluble in water, carbon tetrachloride, ethanol, vegetable oil, acetone, benzene, toluene and chlorinated hydrocarbons; insoluble in mineral oil, mineral spirits, kerosene and gasoline. The amount of wetting agent may be increased to 0.50 part or slightly more but with more than this amount it may sweat out during molding and with amounts below about 0.25 part there is insufficient material thoroughly to effect the other materials. Other nonionic wetting and emulsifying agents of similar characteristics may replace the Antarox to assist in emulsifying the waxes in the resin and to wet the other materials and act as mold lubricants and release agents.

The action of the zinc stearate or equivalent is to impart lubricity to the compound and assist in release of the record from the mold without reducing the softening point of the compound; it is compatible with the waxes and the Antarox. The amount of zinc stearate may vary from about 0.25 to 2.0 parts; lesser amounts do not give the desired lubricity and greater amounts tend to make the compound "cheesy," that is let the record mar more easily.

The carbon black is at once a coloring material and a filler. The preferred carbon black is a channel black with a particle size from 0.010 to 0.017 micron, for instance Kosmos BB or Monarch 74. Other channel blacks with particle sizes from 0.009 to 0.029 may be used but in the case of the larger particle size there is more background noise in the record and the smaller particle sizes are more difficult to disperse in the resin. Furnace blacks from 0.025 to 0.065 micron have been used by the background noise from these blacks is slightly higher and the wear resistance slightly less than with the preferred blacks. There are numerous suitable carbon blacks on the market. About 2 parts of the preferred black give optimum sound and wear but the amount of carbon black may range from about 0.5 to 4.0 parts. Beyond these limits the sound and wear quality of the record decrease.

In making the record molding material the ingredients, preferably in flake or granular form, are mixed and fluxed in a Banbury operated with 160–190 p. s. i. g. of steam on the jackets and rotors. A cycle of 10 minutes for a batch of 120 pounds in a 3A Banbury gave the material a discharge temperature of 195–205° C. From the Banbury, the material was transferred to a 2-roll mill where it was processed for 7 minutes with roll temperatures of 160–165° C., then sheeted off and ground to particle sizes suitable for injection molding.

From this material, 10 inch 33⅓ R. P. M. records were injection molded and wear tested with osmium and sapphire needles by 100 plays in pick-up weights of 7 to 11 grams. The records were characterized by sound and wear qualities superior to records not containing the master-batch mix.

Example 2

The same composition as in Example 1 was made in the same way except that sufficient of the basic polystyrene-silicon carbide mix was used to give a finished record molding material containing 0.035 part of silicon carbide. Microgroove 33⅓ R. P. M. records were molded from this material and tested for 100 plays with both sapphire and osmium tipped needles using 7 to 11 gram pick-ups in comparison with records molded from a similar material in which the silicon carbide had not been processed in a master-batch. The records containing the silicon carbide which had been processed in the master-batch gave less surface background noise both initially and after playing than the records molded from the other material.

Examples 3, 4, 5, 6 and 7

Record molding materials of the following formulae were made by the method of Example 1, that is, by preparing a master-batch, then preparing a basic polystyrene-silicon carbide mix and then preparing the molding material:

Example	3	4	5	6	7
	Parts by weight				
Material:					
Polystyrene	100	100	100	100	100
Carnauba wax	3	3		3	3
Crown wax 1035	3	3		3	3
Crown wax 23			6		
Zinc stearate	1	1	1	1	1
Antarox D–100	0.25	0.25	0.25	0.25	0.25
Carbon black, Kosmos BB	2	2	2	2	2
Carborundum FFFFRA from master-batch	0.02	0.035	0.035	0.025	0.030

All of these materials were molded by injection into 33⅓ R. P. M. records and tested for 100 plays as previously described in comparison with records molded of similar materials in which the carbide had not been processed according to the master-batch system. In all cases records molded from materials containing silicon carbide processed by the mater-batch system had better sound and wear qualities both initially and after playing than did records molded of similar materials wherein the carbide had not been initially processed in a small amount of polystyrene.

Example 8

Compounds, developed primarily for compression molding, of the following formula, were made by the method of Example 1, that is preparing a master-batch, then a basic polystyrene-silicon carbide mix and then the molding material.

	Parts by weight
Polystyrene	100
Carnauba wax	2.5
Crown wax 1035	1.0
Zinc stearate	1.0
Antarox D–100	0.25
Carbon black, Kosmos BB	2.0
Carborundum FFFFRA from master-batch	.025
Diphenylparaphenylenediamine	0.1

In this case the antioxidant was used to protect the material during heating in air on the preheat table; it is not essential but is advantageous. Also, in compression molding compounds, a given percentage of Carborundum has less abrasive action on the needle than the same amount in an injection compound and although master-batched carbide is desirable even in the compression molding compounds, similar compounds containing the undulled Carborundum are superior in sound and wear characteristics to compression molded records containing no Carborundum.

When greater molding plasticity is desired in either injection or compression molding compounds, the fore-

going formulae may be modified by addition of from 1% to 10% of ortho-, meta-, or para-terphenyls or mixtures thereof, or chlorinated bi- or poly-phenyls, for instance Arochlors 4465 or 1254. These modifiers impart increased plasticity to the compound without notably reducing the resistance of the compound to marring. The use of these modifiers also benefits the compounds when the higher molecular weight polystyrene resins are used.

Other modifiers of similar effects are polyethylbenzenes consisting principally of a mixture of di-, tri-, tetra-, penta-, and hexa-ethylbenzenes. The preferred mixture consists principally of the penta- and hexa-ethylbenzenes because of their low volatility and permanency in the record.

When the basic compound is modified to increase its plasticity, by the addition of terphenyls, or Arochlors or ethylbenzenes, a good composition for the production of the relatively large grooved 78 R. P. M. records may be produced by a large addition of relatively soft fillers, for instance, calcium carbonate flour, slate flour, barytes, diatomaceous silica and the like. The range of filler content may be from 10 percent to 75 percent of the weight of the finished composition, the optimum being 50 to 60% when quality and economy considerations are balanced.

The final record composition may also be made by preparing an aqueous emulsion of the waxes and an aqueous emulsion of the resin (except for the resin used in the master-batch and in preparing the basic polystyrene silicon-carbide mix) mixing these emulsions together with the carbon black and Antarox D–100, drying, grinding and then using the ground product with the proper amount of the basic polystyrene-silicon carbide mix, the zinc stearate and such fillers as may be desired to give the molding materials of the foregoing formulae. The final molding materials may be compounded on a 2-roll mill or in a Banbury or a twin screw compounder, for instance a Welding Engineers twin screw compounder-extruder. Using the emulsion system an intimate mixture of the very fine emulsified particles of resin and wax is obtained and on drying of this emulsion, the product contains no large particles of wax to excessively lubricate the surfaces of the mixing equipment and thereby prevent quick and thorough mixing of the entire molding composition.

When preparing sound record compositions, other than black, the formulae used will be the same as those shown herein except that colloidal silica will be substituted for the carbon black, weight for weight, and the desired dyes or pigments will be added. The silica to be used is typified by Monsanto Santocel C which has an average particle diameter of 0.030 micron with a permissible diameter of 0.035 micron. The amount of wax in the compound may run as high as 8 parts and still give an acceptable record and where the compound is modified by the inclusion of the extenders for increasing plasticity, for instance terphenyls, chlorinated polyphenyls and ethylbenzenes, the amount of wax may be as low as 2.5 parts by weight per 100 parts of resin.

What is claimed is:

1. In a method of preparing a resinous polystyrene composition suitable for molding into sound records the steps which comprise milling sharp-edged particles of a member of the group of materials consisting of silicon carbide and boron carbide with a small amount of polystyrene resin sufficient to hold the particles together and enable grinding of particles against one another until the sharp edges of the particles are dulled and thereafter milling in an additional amount of polystyrene sufficient to form a homogeneous composition containing up to about 3.5 parts by weight of said dulled particles per 100 parts by weight polystyrene.

2. In a method of preparing a resinous polystyrene composition suitable for molding into sound records the steps which comprise milling sharp-edged particles of a size between 0.1 and 10 microns of a member of the group of materials consisting of silicon carbide and boron carbide with a small amount of polystyrene resin sufficient to hold the particles together and enable grinding of particles against one another until the sharp edges of the particles are dulled and thereafter milling in an additional amount of polystyrene sufficient to form a homogeneous composition containing up to about 3.5 parts by weight of said dulled particles per 100 parts by weight polystyrene.

3. In a method of preparing a resinous polystyrene composition suitable for molding into sound records the steps which comprise milling sharp-edged particles of a member of the group of materials consisting of silicon carbide and boron carbide with a small amount of polystyrene resin sufficient to hold the particles together and enable grinding of particles against one another until the sharp edges of the particles are dulled and thereafter milling in an additional amount of polystyrene sufficient to form a homogeneous composition containing up to about 3.5 parts by weight of said dulled particles per 100 parts by weight polystyrene together with wax and a mold lubricant.

4. In a method of preparing a resinous polystyrene composition suitable for molding into sound records the steps which comprise milling sharp-edged particles of a size between 0.1 and 10 microns of a member of the group of materials consisting of silicon carbide and boron carbide with about an equal weight of polystyrene resin until the sharp edges of the particles are dulled and thereafter milling the mixture thus prepared with sufficient additional polystyrene resin to distribute the particles throughout the resin and give a composition comprising between 0.01 and 0.035 part of the particles per 100 parts, by weight, of resin.

5. In a method of preparing a resinous polystyrene composition suitable for molding into sound records the steps which comprise milling sharp-edged particles of a size between 0.1 and 10 microns of a member of the group of materials consisting of silicon carbide and boron carbide with about an equal weight of polystyrene resin until the sharp edges of the particles are dulled and thereafter milling the mixture thus prepared with sufficient additional polystyrene resin, wax and mold lubricant to distribute the particles, wax and mold lubricant throughout the resin and give a composition comprising between 0.01 and 0.035 part of the particles, from about 2.5 to 8 parts of wax and 1 part mold lubricant per 100 parts, by weight, of resin.

6. In a method of preparing a resinous polystyrene composition suitable for molding into sound records the steps which comprise mixing aqueous emulsions of a wax and of the resin and drying the mixed emulsions, milling the dry mixture with particles of a member of the group of materials consisting of silicon carbide and boron carbide presenting dulled edges, said dulled-edge particles having been prepared by milling particles of a size between about 0.1 and 10 microns with about an equal weight of polystyrene resin until the sharp edges of the particles are dulled, the materials being proportioned to give from 0.01 to 0.035 part of the particles and from about 2.5 to 8 parts of wax per 100 parts, by weight, of resin.

7. A composition suitable for molding sound records comprising a homogeneous dispersion of particles of a member of the group of materials consisting of silicon carbide and boron carbide having dulled edges, said dulled-edge particles having been prepared by milling particles of a size between about 0.1 and 10 microns with about an equal weight of polystyrene resin until the sharp edges of the particles are dulled in a polystyrene resin in the proportion of from 0.01 to 0.035 part of the particles to 100 parts, by weight, of the resin.

8. A composition suitable for molding sound records comprising a homogeneous dispersion in polystyrene

resin of particles of a member of the group of materials consisting of silicon carbide and boron carbide, wax, mold lubricant and a plasticizer of the group of materials consisting of terphenyls, chlorinated polyphenyls and ethylbenzenes, the carbide particles presenting dulled edges, said dulled-edge particles having been prepared by milling particles of a size between about 0.1 and 10 microns with about an equal weight of polystyrene resin until the sharp edges of the particles are dulled and being proportioned to give from 0.01 to 0.035 part of the particles, from about 1 to 10 parts of said plasticizer, from about 2.5 to 8 parts of said wax and about 1 part of mold lubricant per 100 parts, by weight, of resin.

9. A sound record comprising polystyrene resin and particles of a member of the group of materials consisting of silicon carbide and boron carbide having dulled edges, said record containing from 0.01 to 0.035 part of the particles per 100 parts by weight of the polystyrene resin, and said dulled particles having been prepared by milling the particles with about an equal weight of polystyrene resin until the sharp edges of the particles are dulled.

10. In a method of preparing a resinous polystyrene composition suitable for molding into sound records the steps which comprise milling particles of a size between 0.1 and 10 microns of a member of the group of materials consisting of silicon carbide and boron carbide with about an equal weight of polystyrene resin until the sharp edges of the particles are dulled and thereafter milling the mixture thus prepared with sufficient additional polystyrene resin, wax, mold lubricant, and a member of the group of plasticizing modifiers consisting of terphenyls, chlorinated polyphenyls and ethyl benzenes to distribute the particles, wax, mold lubricant and said modifier throughout the resin and give a composition comprising between 0.01 and 0.035 part of particles, from about 2.5 to 8 parts of wax, 1 part of mold lubricant and from about 1 to 10 parts of modifier per 100 parts, by weight, of resin.

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