

ANTI-STATIC PHONOGRAPH RECORDS

SINCE THE ADVENT of 45's and L.P.'s, record users have become acquainted with static electricity on disk surfaces causing accumulations of dust and lint in star-like patterns and swirls. Attempts to remove the dirt usually result in a scratched surface of inferior playing quality.

Static electricity has been blamed unjustifiably for some record troubles. Reference is sometimes made to ticks and pops in the sound grooves as being due to the discharge of static electricity from the plastic surface to the cartridge or tone arm. It is doubtful if this is true. Usually these sounds are caused by surface imperfections resulting from poor molding in the factory or mishandling and scratching during use by the customer.

The plastic materials normally selected for use in the manufacture of records are notorious in their ability to by G.P. HUMFELD, Mgr.,
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pick up and hold for a long period of time a high static charge. Usually, the higher the record quality the purer the composition, and therefore the greater the static charge. This has been unfortunate as far as the customer is concerned.

The first strong charge is created on a record at the time of its manufacture. It develops at the moment when the record is separated from the surfaces of the cavity in which it is molded. In the hands of the customer, additional charges can be built up by pulling the record out of its jacket. Therefore, without some permanently effective method of reducing the disk's static

charge the customer is continually confronted with it as a problem.

ANTI-STATIC METHODS

Over the years, many gimmicks have been placed on the market to minimize or eliminate the tendency of a record to pick up and carry a static charge.

First in this category is the large group of wetting agents or detergents. These can be mixed in minute quantities with tap water (about a 1-percent solution, or a teaspoon to one quart of water) to make up a wiping solution. A lint-free cloth moistened with this solution will effectively clean disk surfaces and impart some anti-static effect. Its effectiveness is limited to relative humidity values above 35 percent. It has no lasting value, because a cloth dampened with water alone will wipe off most of the coating.

Other devices depend upon air ioniza-

Fig. 1—(Background photo) Electron microscope view of conductive carbon black.

Fig. 2—(Insets in Fig. 1) Vinyl particles, showing difference in particle shape between suppliers A, B, and C.

tion to reduce the static charge on a record. They employ materials like polonium in combination with a brush which removes the dirt as the record surface and particles are freed of their charge.

Work on anti-static records started almost as soon as L.P.'s and 45's appeared on the market. Three general methods of attack were employed: 1) Coat records with films which would improve surface conductivity to the point where the records would not hold a charge. 2) Mix into the record plastic a conductive carbon black following the principles used in making molded rubber articles conductive. 3) Mix into the record compound a material which possessed only limited compatibility with the ingredients in the mix; by careful control of the quantity added to the mix, a controlled bleed-out might reduce surface resistivity to the point where anti-static properties could be obtained.

THIN-FILM COATINGS

Considerable time was spent on method one. Records were coated with thin films of such materials as titanium tetrachloride, platinum chloride, and tin chloride. None of these produced films that were effective in reducing surface conductivity.

An attempt was made to sulfonate a vinyl record surface in a manner similar to that performed on polystyrene records, as described in U.S. Patent 7,727,831. Sulfonation did not occur under short exposures. Time intervals in the order of 20 minutes at temperatures of 120° to 140°F reduced surface resistivity, indicating that sulfonation might have occurred. The vinyls, however, decomposed under this severe treatment in concentrated H2SO4 and then in 20-percent NaOH. It may have been the resulting decomposition products which reduced the resistivity values.

A number of surface active agents were evaluated (see Table I). Records were treated by dipping them in 0.1-, 1-, or 10-percent solutions of the various materials. This was followed by a dry spinning step. Surface resistance was measured using the method described in ASTM designation D-257-52T.

The surface resistance at which a coating is effectively anti-static at a particular humidity is not specifically known. The literature contains many references ranging from very low values for surface resistance to fairly high values at which a surface may be considered anti-static. Therefore, we have

TABLE I SURFACE RESISTIVITY, OHMS

Product	Relative Humidity, %	Surface Resistivity, ohms, at Various Concentrations in Water		
		0.1%	1%	10%
Niatex AG-2	10 52	$6 \times 10^{13} \ 3 \times 10^{13}$	$3 \times 10^{10} \\ 5 \times 10^{11}$	$6 \times 10^{8} \\ 2 \times 10^{9}$
Tergitol Nonionic TMN	10 52	$7 \times 10^{15} \\ 7 \times 10^{14}$	$3 \times 10^{15} \\ 3 \times 10^{14}$	$8 imes 10^{12} \ 8 imes 10^{12}$
Tergitol Nonionic NPX	10 52	$8 \times 10^{15} \ 6 \times 10^{15}$	$^{4} imes 10^{14} \ 8 imes 10^{14}$	$^{6 imes10^{12}}_{7 imes10^{11}}$
Tergitol Nonionic NP-27	10 52	$1 \times 10^{16} \ 1 \times 10^{16}$	$5 \times 10^{15} \\ 6 \times 10^{14}$	$2 \times 10^{13} \ 3 \times 10^{12}$
Carbowax 200	10 52	$1 imes 10^{16} \ 1 imes 10^{16}$	$1 \times 10^{16} \\ 8 \times 10^{14}$	$1 \times 10^{13} \ 1 \times 10^{13}$
Propylene Glycol	10 52	1×10^{16} 1×10^{16}	$^{1}_{1} imes ^{10^{16}}_{10^{16}}$	$1 \times 10^{16} \\ 1 \times 10^{16}$
Ucon Lubricant 50-HB-3520	10 52	$1 \times 10^{16} \\ 8 \times 10^{15}$	$3 \times 10^{14} \\ 1 \times 10^{14}$	$2 imes 10^{13} \ 3 imes 10^{12}$
Ucon Lubricant 50-HB-55	10 52	$1 \times 10^{16} \\ 1 \times 10^{16}$	$1 \times 10^{16} \\ 1 \times 10^{16}$	$8 \times 10^{14} \ 8 \times 10^{14}$
Zelec DP	10 52	$1 \times 10^{16} \\ 8 \times 10^{15}$	$1 \times 10^{13} \\ 6 \times 10^{10}$	$^{4}_{1} imes 10^{10}_{10}_{109}$
Zelec DK	10 52	$^{4 imes10^{15}}_{1 imes10^{14}}$	$3 \times 10^{12} \\ 2 \times 10^{11}$	$5 \times 10^{10} \ 9 \times 10^{8}$
Zelec NE	10 52	$6 \times 10^{15} \ 3 \times 10^{15}$	$2 \times 10^{17} \\ 6 \times 10^{11}$	3×10^9 8×10^8
Zelec NK	10 52	$1 \times 10^{16} \\ 5 \times 10^{14}$	$^{7}_{6} imes ^{10^{10}}_{10^{12}}$	$4 imes10^9\ imes10^9$

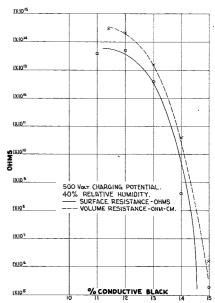


Fig. 3—Resistance of record compound with 11 to 15 percent of conductive carbon black.

assumed the arbitrary range of values of 10° to 10¹¹¹ ohms as being low enough to produce desirable anti-static properties for phonograph records. Using this range of values as a tentative standard, none of the materials listed in Table I were effective in 0.1-percent solutions at low humidity. Coatings of Zelec NK (E. I. du Pont Co.) from 1-percent solutions were effectively anti-static, but were badly stained and were wiped off readily with a damp cloth. From this work it was felt that a coated record would not give the high quality antistatic disk desired.

CARBON-BLACK MIX

Method two, employing the use of a conductive carbon black, was investigated quite thoroughly. The so called acetylene blacks and high-structure furnace blacks were employed in this study. An electron microscope view of this type of carbon black is shown in Fig. 1. Experience showed there is a threshold loading that must be reached before any conductivity can be obtained. This value appears to be around 13percent (by weight) loading of these special blacks in the plastic material. From this value, further loading improves conductivity, as shown in Fig. 3. Unfortunately, this type of formulation presents many difficulties: 1) it is extremely slow to fuse in a banbury mixer; 2) the presence of the carbon black reduces the strength and flexibility of the plastic composition below the normally accepted safe values; 3) the audio properties of disks made from such a mix are poor because of a steady hiss caused by the carbon black

in the plastic and 4) it is extremely difficult to mold into perfect L.P. records. Anti-static properties were very good. Surface resistivity values of around 9×10^6 were measured. In spite of the good anti-static properties, this method was rejected as not being commercially feasible.

CATIONIC MATERIALS

Method three was the only alternative left that showed any possibility of success. More than 100 different materials have been tested over the last ten years as possible ingredients for milling into a vinyl record mix to reduce surface resistivity to a satisfactory value. Greatest success was obtained from a family of cationic materials supplied by the American Cyanamid Company. It was established rather early in the work that a quaternary ammonium salt gave the best compromise between compatibility and limited bleed-out to the disc surface necessary to produce this antistatic effect. Catanac SN was selected as being the most effective member of this family of compounds. American Cyanamid indicates its structure is as follows:

stearamidopropyldimethyl- $\beta\text{-}hydroxyethylammonium\ nitrate}$

A concentration of about 1.3 percent by weight mixed into the resin seemed to give optimum results. Tests in the factory however, showed it could not be added directly in the banburys to get a sufficiently uniform mix to produce good records. Stains were encountered on the record surface and very spotty noise in certain portions of the record indicated that a better mixing procedure was needed. The leading vinyl sup-

pliers were called in and shown the problem. The request was made that they attempt to coat their resin with the agent during manufacturing to get a uniform coating on each particle of material. Each one achieved some degree of success in this work. However, particle shape plays a very important part in this process. Fig. 2 shows the difference in particle shape between suppliers A, B, and C. Experience has shown that coated materials like B and C tend to cake or block during storage. This causes handling difficulties in the compound plant. On the other hand, supplier A has produced a dry, freeflowing powder that processes without difficulty. More recently, work on the part of other vinyl manufacturers has shown that several of them have been able to modify the particle size distribution and shape of their resins to such an extent that they can supply a coated resin which is dry and free flowing.

COATED-RESIN PRODUCTION

The first production lots of coated resin were made available for test in early 1959. Results were promising, but refinements were needed to put the product on a commercial basis. An unofficial committee consisting of Steve Ransburg of our own engineering staff (now Manager of Manufacturing in the new Magnetic Tape Plant of the Record Division), Steve Crum of Union Carbide Plastics Company, and Frank Miner of American Cyanamide set up a crash program using the full support and know-how from each organization to solve the remaining problems and carry out the refinements necessary to make a fully commercial product. A series of runs were made to determine the upper and lower control limits of the Catanac SN content. Banbury cycles and processing temperatures were studied to determine their effect upon the anti-static properties. Formulation modifications were

made to determine the effect of different types and concentrations of carbon black and heat stabilizer upon the antistatic properties.

In a three-month period extending from April through June, most of these points were evaluated and a satisfactory product was developed so that production could get underway by July 1, 1959.

Recognition should be given to Amel Vitalis and others of the American Cyanamid staff who developed analytical procedures for measuring the catanac content of the resin and who aided in the evaluation of surface molding imperfections caused by the presence of the Catanac SN. Recognition also goes to George Graeber of Union Carbide Plastics and his staff at Texas City for their efforts in learning how to produce a uniformly coated resin of high quality. In our own organization, recognition should be given to all people connected with R. O. Price's organization, who worked so diligently to make this crash program come to a successful ending.

SUMMARY

To the customer, for whom we all really work, we have given the following:

- 1) A record, labelled *Miracle Sur-* face, which is free of static charge;
- A record which will not attract and hold lint and dust to its surface:
- A record capable of being easily cleaned of lint and dust which may settle out on it when left lying out unprotected;
- 4) A record that will have better sound qualities over a longer period of time in the hands of the customer because of the freedom from lint and dust; and
- 5) Another "first" to the consumer under the name of RCA.

GEORGE P. HUMFELD graduated from Purdue University in 1937 with a B.S. degree in Chemical Engineering. He worked as a chemist in a nonferrous foundry for five years after graduation and then joined U.S. Rubber Company as a rubber compounder during the war years. He joined RCA in 1946 as an engineer in the Record Compound group and in 1947 was appointed group leader. In 1956 he was appointed Manager of this group. He is a member of the American Chemical Society and the Society of Plastics Engineers.