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AROCLOR

Referring to your request for us to study past literature, patent and otherwise, with regard to the AROCLOR chlorinated polyphenyls, and to thereafter indicate the possible areas in which Monsanto might gain a new "patent position" in the field of chlorinated biphenyls, we present the following for your consideration:

Patents relating to chlorinated biphenyls go back at least as far as 1931, when a patent (U.S. 1,836,180) was issued to McCullough and Jenkins and assigned to Swann Research, Inc., claiming a dielectric comprising a mixture of chlorinated diphenyl having a number of stated physical properties. Chlorinated diphenyl was, of course, known before 1931, which accounts for the "use" type claims of this early patent.

Monsanto acquired the AROCLOR products by purchasing Swann Research in 1935. At that time Swann owned about twenty-two patents relating to the AROCLOR products, all of which are now expired, embracing the following: A chlorinated diphenyl composition containing a minimum percent chlorine, processes for producing chlorinated diphenyls, and the use of chlorinated diphenyl in the following ways: As a dielectric (mentioned above); as a varnish resin; as a cement in the manufacture of shatterproof glass; as a substitute for shellac in sealing wax; as a non-discoloring waterproofing agent; as a synthetic resin; in varnishes; in lacquers; in emulsions; as a transparent film for photographic coatings such as with cellulose acetate; as an adhesive when mixed with a plasticizer; as a white pigment in paints; to coat casein plastic in order to provide a transparent wrapping material; and in combination with sulfur to provide a binder for cellulosic fillers for the production of molded articles.

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After acquiring Swann, Monsanto continued an active research program with respect to chlorinated diphenyls, Thus, patents have been obtained by Monsanto which embrace a process for the chlorination of nitro-substituted diphenyls, dielectric compositions, label adhesive compositions employing chlorinated terphenyls, an adhesive for polystyrene resin tile, a process for separating the various materials obtained in the production of diphenyl, the use of terphenyls as a plasticizer for waxes (as paraffin), polystyrene-chlorinated diphenyl compositions, mixtures of meta- and para-diphenylbenzenes, an improved process for producing biphenyl, and in the dielectric field, chlorinated diphenyls have been used in combination, for example, with chlorotoluenes, ortho- and para-diphenylbenzene, chlorinated ortho-nitrodiphenyl and chlorobenzenes.

Additives for the scavenging of residual HCl which have been used in the AROCLOR products for dielectric purposes are zinc dithiocarbamate and its substituted derivatives, aluminum isopropylate, aminated-N-phosphoryl-o-aminobiphenyl, organic antimony compounds, morpholine and its substituted derivatives, organic tin thionyl compounds, dibutyl diphenyl tin, tetraphenyl tin, ethyl silicate, 2,4-diaminodiphenylamine, o-anisidine, p-anisidine, p-nitroaniline, mono-ortho-tolyl biguanide and diphenyl tin diethylate.

Some of the known applications for the AROCLOR products include the following: In adhesives, in electrical equipment, as a fluid-actuating medium in such articles as thermostats, as hydraulic media, a heat-transfer media, as lubricants in such things as compressors, in the graphic arts as a pigment vehicle, in the impregnation of wood, paper, cloth, etc., to impart moisture and gas resistance, flame resistance, lubricating qualities, etc., as a pigment for various plastics, in paints and varnishes, in rubber as a plasticizer, in the vinyl resins as a plasticizer, in nitrocellulose coatings and in waxes as an extender.

AROCLOR products have been the subject of patents issued to others than Swann or Monsanto. Thus there have been

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"outside" patents on the AROCLOR products in the following areas: As a softener in a solvent-type metal coating composition, in flame-retardant polyethylene compositions, in vinyl chloride compositions to provide fireproofing, in fire-retardant coatings made from acrylic and methacrylic acids, in a lining composition for lining the ends of anti-freeze containers, as a binder in flameproofing compositions for textiles, as a plasticizer for plastic floor tiles, in linear polyamide compositions, in vinyl lacquers, in chlorinated isobutylene polymer coating compositions, in fire-resistant linoleums, in polyvinylacetal coatings, AROCLOR with para-coumarone-indene resin to make an adhesive, as a moldable composition with polystyrene for making electrical insulators, as a delustering agent for cellulosic, silk and rayon fibers, in moisture- and fungus-resistant hot metal coating for electrical equipment, in a wood waterproofing composition, in anti-static coatings for plastics, in water-based vinyl acetate-maleate copolymer adhesives, in pressure-sensitive record material compositions, in rubber compositions, in combination with powdered metals as a glazing compound, and as a vehicle for floor polishing compositions composed mainly of a copolymer of cinnamic acid and an acrylic acid.

The foregoing is presented in order to clearly bring to the forefront the impressive array of "prior art" staring us in the face with regard to re-establishing a basic patent position in the AROCLOR field. With the above in mind, we believe the following to be worth considering from a Research-Patent standpoint:

I. AROCLOR per se

A. Process and Synthesis Studies

1. Interest in the composition of the AROCLOR products is shared by Monsanto and our customers. Dayton is working to identify the isomers and compounds in AROCLOR 1242 especially. Mere identification of the isomers and compounds, however, would not

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provide patentability since inherently the composition has not changed, nor have the various properties changed. Though possibly not desirable because of the difficulty in enforcing such a patent, the method of identifying the isomers and compounds, if novel, might be patentable.

2. After methods are developed for the identification of the isomers and compounds in AROCLOR, a project is planned whereby the properties of the AROCLOR products, such as pour point and dielectric constant, might be improved by changing the process in order to produce a greater quantity of some isomers. Potential areas of study include the following:

   (a) Treatment of AROCLOR with $AlCl_3$ or other agents.

   (b) Chlorination in liquid phase with other catalysts.

   (c) Chlorination at high temperatures in liquid state.

   (d) Vapor-phase chlorination.

   (e) Addition chlorination followed by dehydrohalogenation.

   (f) Chlorination in a solvent.

   It is certainly feasible that patent protection could be obtained on a process which provides for changing the usual isomer ratios.

3. Another phase of the Dayton work would be the isolation of various isomers of AROCLOR in order to study the dielectric properties

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and stability of each. Those isomers which would contribute to the improvement of the dielectric properties of AROCLOR could possibly be synthesized and added to a "normal" AROCLOR or possibly used alone. At present there is a disclosure pending at Dayton for high dielectric constant compositions, which compositions are each composed of two specific isomers. The enhancement of dielectric properties of the AROCLOR products by the addition of certain isomers or the use of ether materials could certainly be expected to be patentable.

4. As a result of the process studies at St. Louis last year, including definition of catalyst concentration and optimum chlorination temperature, we are now able to maintain the unstable chloride concentration of the AROCLOR products below 2 ppm, which is most desirable for dielectric uses. Such an improved process is potentially patentable, and an application should be filed.

5. The continuous chlorination process which was demonstrated at Anniston last November might have some patentable features. At least a review of the process should be made by the Patent Department in view of the interest in improving our patent position. (See Organic Division Report No. 1530 and F-688, Job No. 2-02-750.01-3040, and also Organic Division Report No. 2036, Job No. 2-02-750.01-3192.)

6. Previous patents on the AROCLOR process are very uninformative so that any new concise data on any chlorination process might be given consideration by the Patent Office. For instance, Patent No. 2,019,015 (Swann

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Chemical Co.), on the vapor-phase halogenation of diphenyl, does not characterize the product or products in any way. Thus, any work to define this mode of chlorination or the products produced may be patentable.

B. Application Studies

1. Applications of the AROCLOR products have, in the past, been largely centered around the area of fire-resistant functional fluids which contain AROCLOR in combination with various materials, such as phosphates, HB-40, adipates and silicates, as well as small amounts of materials added as V.I. improvers. At present, there is a development in this area in the utilization of AROCLOR 1242 and AROCLOR 1248 plus lubricity agents to provide a synthetic lubricant, for example, the new fluid designated as OS-95. Looking to the future, it appears that the use of AROCLOR plus additives could replace a portion of the mineral oil plus additives field. A patent application should be filed on the OS-95 composition as well as other synthetic lubricating compositions which develop. Although this field is just now being explored, it certainly offers a potentially bright patent picture if commercialization of such compositions can be realized, since the use of additives in AROCLOR for such uses is a new field.

2. At various times AROCLOR products have been used as secondary plasticizers, as, for example, in combination with SANTICIZER 160. Patentability is slim in this area.

3. The Dayton Patent Department presently has disclosures relating to the preparation of

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coating resins by the reaction of diglycidal ether of hydrolyzed AROCLOR, benzoic acid and fumaric acid, and cross-linking with styrene and the use of the AROCLOR line as perfume stabilizers (fixers).

II. AROCLOR Derivatives and Modifications

1. AROCLOR products will undergo various reactions, involving the chlorine group, under the proper conditions. Dazzi, at Dayton, has hydrolyzed AROCLOR 1268 and others to give a difunctional dihydroxy compound. Patent applications are being considered which will cover the method of making hydrolyzed AROCLOR and its uses. However, Progil, of Paris, has a British patent (No. 779,221) on this subject. These phenolic derivatives have been tested as bacteriostats and have some activity which might warrant an application. Dayton has two disclosures in this area, one relating to diglycidal ethers of hydrolyzed AROCLOR and the other relating to the preparation of fatty acid esters of diglycidal ether of hydrolyzed AROCLOR.

2. AROCLOR products will react with ammonia and amines under proper conditions. Some work has been done at Dayton along these lines, and patent applications for these materials might be filed.

3. The cyano derivative of AROCLOR 1242 has been made. A high dielectric constant product was obtained, but the material was highly contaminated. (See Organic Division Report No. 1677, Job No. 2-02-750.01-2678, by J. K. Sears.) More work in this area might provide the basis for a patent application.

4. Alkyl chlorobiphenyls have been made by alkylating AROCLOR products. (See Organic Division Report No. 1184, Job No. 2-02-750.01-2682, by W. W. Marshall.) The products

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obtained were tested as plasticizers, but showed no promise. Also, it was concluded that no advantage is offered in regard to viscosity by replacing one chlorine with an alkyl group. A British patent (No. 501,745) to duPont exists on the chlorination of alkyl biphenyls. Even though alkylated AROCLOR products are old as such, specific new alkylated AROCLOR products might be patentable if a utility for them could be found and if they had unusual properties as compared to the known alkylated AROCLOR products. Also, an improved or new method of alkylation might be patentable.

5. Attempts to sulfonate AROCLOR products, or to make the sulfonyl chloride derivative, have not been too successful. The AROCLOR products can be nitrated as evidenced by U. S. patent 2,358,628 to General Electric Company. A similar patent to Monsanto, U.S. 2,370,113, describes the chlorination of nitrobiphenyl. Nothing patentable is apparent in this area at present.

6. A further reaction that might be of interest is that of an AROCLOR and phosgene. Possibly a fluorene derivative could be obtained. Since such work is basic, a patent on new compounds might be obtained, assuming a utility for the compounds could be found or at least an improved process for making fluorene.

7. With alcohols or phenols under proper conditions, ethers can be obtained. Some work was done at Dayton in 1954 which might provide some basis for patent applications.

8. The above reactions have been simple reactions involving, in many cases, a chlorine group. No doubt, there are many other possible reactions that could be studied involving the biphenyl ring which could yield patentable inventions.

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III. Miscellaneous Biphenyl Derivatives

1. Many patents exist on the common derivatives of biphenyl, and numerous derivatives are reported in the literature based on biphenyl and terphenyl. However, many of these pure compounds are made indirectly. The isomer problem found in the separation and utilization of all the isomers will always be present with biphenyl as a starting material. Thus we find limited use of biphenyl for making pure compounds. The field is open for exploitation. Inquiries for the monochlorobiphenyl isomers indicate an interest in these compounds as raw materials for other compounds. Although we already have expired patents on producing these compounds, further work might be profitable for patent applications not only in the chloro compounds but in derivatives of and from the compounds. The question of patentable subject matter would have to be explored if and when new derivatives were made. Utility might be a problem.

2. The possibility of introducing functional groups in order to make the mono- and di-derivatives of biphenyl would present a challenge to a good exploratory chemist. Some sulfonic acid, hydroxy, carboxylic acid, aldehyde and ketone derivatives have been reported. Patentability would again depend upon utility.

IV. New Dielectrics to Replace the AROCLOR Products

L. A new dielectric based on a good stable, cheap compound other than biphenyl does not seem likely at present. Monsanto was licensed by Federal Telephone and Radio Corporation (subsidiary of IT&T) to produce a dielectric based on chlorinated alpha-methylstyrene dimer (1,1,3-trimethyl-3-phenyl indane) under U. S. Patents 2,552,607 and 2,552,608, but no success was attained in marketing the product. Monsanto Case 1328 (St. Louis), covering a chlorinated

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trimethyl and tetramethyl phenyl indane, is also pertinent. Thus, the approach of using a new base raw material is not commercially promising, even though patents on new materials might be obtained.

2. The approach mentioned above, of using an additive in the AROCLOR products, may be the most fruitful means of keeping the AROCLOR products in the forefront. Westinghouse (U.S. Patent 2,434,540) is working with the addition of tolyl xylyl sulfone to the AROCLOR products to increase the dielectric constant and to give a more compact capacitor. General Electric has U. S. Patent 2,410,714 on the use of certain sulfones with AROCLOR products for a similar use. Many patents are held by General Electric on AROCLOR products in combination with additives for use on capacitors, but none are exploited commercially. Also, combinations of an AROCLOR and additive for transformer fluids have not been commercialized. Apparently there is no great demand for such products to justify further work. The obtaining of patents would, of course, depend upon research in this area.

From the foregoing, it is our conclusion that there are only some limited areas still open in which patent coverage might be obtained.

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