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PROCESS FOR THE PRODUCTION OF

AROCLORS, PYRANOLS, ETC.

AT THE ANNISTON AND AT THE WM. G. KRUMMRICH PLANT

April 1955 ---------- E. Mather

Distribution List (amended July 19, 1956)

1. Mr. J. S. Brough, London
2. Dr. N. B. Dyson, Newport → Newport T.I.E. file
3. Mr. G. V. Taylor, Newport
4. Mr. G. V. Taylor, Newport → Newport Process Superintendent
5. Mr. W. E. Hamer, Ruabon
6. Mr. J. F. Stickley, St. Louis → Krummrich Plant
7. Mr. J. F. Stickley, St. Louis → St. Louis Library
8. MCL file at St. Louis
9. Mr. D. B. Hosmer, Anniston
10. Spare held in M.C.L. file at St. Louis
11. Dr. W. A. Hayward's file Ruabon

also Section IX, Specifications and Test Methods, to Newport Analytical Department.



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VI. PROCESS IN DETAIL, contd.

Packing

The finished Aroclcrs are run off into drums, a piece of diaper cloth being tied on the pipe outlet for the lighter Aroclors, and a piece of fine gauze for the heavier Aroclors, which have to be handled hot.

This, of course, is to arrest stray bits of pipe scale etc., but the precaution is now omitted at the Krummrich plant when materia are being filled directly from the delivery of the filter. Newpo arrangements for filling and weighing drums are discussed in Lond Engineering Final Report, September 1951, page 1D8 and 1 F3-10, also in the start-up reports, July 24, and September 27, 1951.

The drums must be clean and dry, especial care being needed with electrical grades. Newport complaint NF/61, November 1951, of turbidity in 1248 was traced to the presence of water in the drums Apparently, in presence of water, the Aroclor reacted on the galvanizing of the drum. Newport plant report, December 1951, mentions the installation of equipment for drying the drums.

Care is taken not to do any packing if there is HCl fume in the ai

The gaskets for the bungs of the drums have to be correctly chosen A sample of the gaskets supplied by the Melrath Supply & Gasket Co to the Krummrich plant was sent to MCL, April 1947. See also the discussion of gaskets on page 2, Section XII, below.

Mr. Pemberton, December 1950, collected samples of the labels used at the Krummrich plant; one a patent list label, and the other a warning label on toxicity.

The effect of exposure of Aroclors to metal contact is discussed ir Section VII, comments, page 17 below. Generally speaking, the distilled Aroclors are packed in galvanized drums, the undistilled ones in black steel drums. Flaked or milled solids were packed in barrels or Leverpac containers, bulk solid or resinous Aroclors go out in friction type lid drums, (galvanized for the distilled grades). Storage and blending of the distilled Aroclors is done in steel vessels sprayed with tin or zinc, or aluminum lined.

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VI. PROCESS IN DETAIL, contd.

Packing, contd.

Since the Aroclors are such effective solvents , they damage, an are damaged by, ordinary paints, lacquers, insulating varnishes, This feature is important in connection with hydraulic fluids containing Aroclors. See, for example, MCL Research Progress rep 1151, DF 54/26/7 and DF 54/277/6 and 1152 DF 4/16/7 and 8 July 19 etc., also the Section III, Physical & Chemical data, above. Dru for electrical grades of Aroclors are not painted.

Newport Plant Technical Committee meeting, April 14, 1953, page 2 reported some promising tests with lacquered drums for electrical grades. It was decided not to use lacquered drums for resinous Aroclors on a returnable basis, because the lacquer suffered at the high temperatures likely to be used in melting the material f the drums.

Aroclors also are dispatched in rail cars. At the Krummrich plant the manhole of the car is protected by a tarpaulin tent during fil Newport plant report for July 1954 mentions the installation of tank-filling facilities. The Krummrich plant operating instructio August 10, 1954 mention that rail cars for Pyranols and Aroclors are insulated and have either a steam coil or a steam jacket. The are lined with Aluminium or else sprayed with tin and zinc. Only dry air is used for unloading. MCC have a "Christmas Tree" fittin a one piece fitting carrying air valve, dip pipe, release valve and pressure gauge, for use on rail tanks. It is important to dra the coil or jacket of the rail tank in cold weather. Galvanized or lacquered drums are used for Pyranols.

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XI. HAZARDS.

Toxicity

There are many literature references* to harmful effects of the ty of "chlor acne" resulting from exposure to chlorinated diphenyls, especially in cases where people working with small electrical co ponents have been exposed to the fumes of hot, highly chlorinated Aroclors. Chlor acne is sometimes accompanied by gastric troubles, and there are literature references to liver troubles.

There was some trouble of this kind among the production workers Anniston in the early days of the development of the Aroclors. A that time highly chlorinated Aroclors were being made from diphen which had come from low grade benzene. Since good benzene has be used, the same Aroclors have been made without trouble. In March it was reported that the Anniston diphenyl and Aroclor plants had 12 years without lost time accident.

From the start of Aroclor manufacture at the Krummrich plant the operators have been supplied a clean change of clothes every day, and time has been allowed at the end of the shift for bathing. Operators are advised to wash hands and face before eating. The Anniston operators do not have the same issue of clean clothes.

* Percy May, "Chemistry of Synthetic Drugs" , 3rd edition, page 1 The "Chemist Analyst", September 1947, Volume 36, No.2 page 33 and a report by Dr. M. G. Lester, Anniston plant, 1937, give da on the toxicity of diphenyl.

MCC Bulletin P-115 (new edition) mentions 0.5 to 1.0 mg. per cbm in air as th highest safe concentration of higher Aroclors, and 10 mg. for more highly chlorinated Aroclors.

H. B. Edkins "Chemistry of Industrial Toxicology", page 149 give 0.5 to 1.0 mg. as the allowable limit in working rooms.

The MCC Bulletin "Physical Properties of Aroclors" mentions sys temic effects arising from the oral injection of Aroclors.

See the letters, E. Mather to P.J.C.Haywood, December 17, 1951, Mather to Newman, January 8, 1952, reviewing the literature on toxicity of Aroclors.

See also correspondence relating to the article in Chem. & Eng. May 17, 1954, pages 2038 -, and the warning labels mentioned on page VI-34 above.

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XI. HAZARDS, contd.

St. Louis, Main Office

cc: Mr. W. E. Hamer, Ruabc
Mr. W. H. Ritchie, Rua
Dr. H. R. Newman, Ruab
Mr. S. M. Kulifay, Kru
Dr. D. S. Weddell, St.
Mr. F. T. Marshall, St

December 11, 1951

Mr. P. J. C. Haywood

Newport (Airmail)

AROCLORS::TOXICITY

Since writing to you on December 3rd I have come across a letter of mine to Mr. W. M. Cooper, London, June 24, 1948, (copies to W.D.S., W.H.G., and others), calling attention to an article in the J. T. Baker Company's "Chemist Analyst", Volume 26, No. 2, page 33, September 1947.

I attach a copy of this article, and I think you will agree that the warning relates only to really bad exposure, not such as should occur in ordinary analytical work.

On October 27, 1947 Mr. Barbre of the Krummrich plant sent a copy of the Journal to Dr. Jenkins at Anniston for comment. Dr. Jenkins did not make any comments at the time but the following extract from Mr. Barbre's letter is interesting:

> "During the 11 years of production here only one man evidenced dermatitis. He had also shown similar symptoms in several other departments. When making Aroclor #1270 which is flaked, a noticeable amount of fine fume solidifies in the air. If men are exposed to it during hot humid weather, the skin is irritated, but we have not had any difficulty in curing cases of dermatitis from it".

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The Chemist Analyst, Vol. 36, No. 2, page 33,
J. T. Baker Chemical Co., Phillipsburg, N. J.
September 1947

ON THE TOXICITY OF THE "AROCHLORS" (sic)

Robert M. Brown, Chief
Industrial Hygiene Section, Division of Health
Dept. of Public Welfare, City of St.Louis, Mo.

A recently published article (Maglio, M. Martin, Chemist Analyst, 35 94 (1946)), has recommended the substitution of one of the "Arochlors" as the melting-point bath liquid in preference to the customary sulphuric acid. As stated in that article "Arochlors" are a group of chlorinated diphenyls produced by the Monsanto Chemical Company.

There is need therefore to give warning. For the toxicity of these compounds has been repeatedly demonstrated, both from the standpoints of their absorption from the inspired air, as well as from their effects in producing a serious and disfiguring dermatitis when allowed to remain in contact with the skin. Since these effects have been repeatedly observed, industrial hygienists have taken care to see that the proper controls have been established wherever these products are used. For example, the maximum allowable concentration of chlorinated diphenyl for an 8-hour working day is 1 milligram per cubic meter of air.

It is probable that nothing like an uncontrolled industrial exposure will occur in the laboratory. However, whether an individual is subjected to a possible acute exposure to chlorinated diphenyl, and its serious consequences, will depend upon the size of the melting-point bath, the caution with which it is used, and the temperature to which it may be heated. Likewise, with careless handling of the material and the resulting contamination of the skin, clothing, laboratory towels, work table surfaces, etc. the way is left open for the producing of dermatitis. Scrupulous cleanliness must be insisted upon wherever this material is handle

The foregoing remarks have been prompted by the belief that in recommending the use of a material with which is associated a potenti hazard from the health standpoint, it is very important that the possible consequences be presented together with recommendations fo correct handling.

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XI. HAZARDS, contd.

Mr. A. C. W. Pennington of Newport, reporting on his American tour, December 29, 1950, page 5, writes:

"HEALTH AND SAFETY":

"At Anniston, no special protective clothing is provided the Diphenyl and Aroclors operators. A daily change of clothir was provided in the past but this practice ceased before the wa Gauntlet leather gloves and face shields are, of course, availa as required on the plant.

" Tins of cold cream ointment, theatrical quality, are to in the building, but the application of the cream is left to th operator's decision of the job in question. The men are expecte take a bath, in their own time, at the end of the shift. A goo quality soap, and alcohol for rubbing down purposes, are provid The operators are sufficiently trained in the need for personal cleanliness that a record of bath taking is not warranted.

"Emergency showers are provided on each floor of the Diphe building and safety notices are widely used.

"At St. Louis, Plant B, the Aroclors building is rated a toxic department. Each operator is provided with a complete set of clothing comprising hat, coat, trousers, combination under-clothes, socks and rubber shoes. A clean change of clothing, except shoes, is placed in the operator's locker in time for the following shift. Men working extra shifts are given a clean set of clothing. Canvas gloves and goggles are provided and 'Ply' hand barrier cream is available for use when necessary.

"Twenty minutes' paid time is allotted for bathing at the end of the shift but, again, no record is kept that baths are actually taken. Theoretically, food is not allowed to be eaten within the Aroclors building. Instructions are issued that hands and face should be washed well before eating.

"Employees in toxic departments are given an annual medical examination and a lung X-ray every three years.".

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XI. HAZARDS, contd.

Toxicity, contd.

A good deal of work has been done on determination of the vapour pressure of the Aroclors, and on the determination of concentrat of Aroclors in air. See pages 9-, Section III, above, for a sum of this work.

In 1950 (letter April 20, N. F. Rapps to E. Mather) the Admiralt expressed interest in the determination of micro-quantities of Aroclors. MCC have a method for the determination of traces in air by means of the "Halidometer".

Mr. Ellenburg, March 15, 1954, mentions work done by H. B. Richa Jr., of MCC, June 17, 1953, on the determination of the concentra of Aroclors in air. Mr. Ellenburg also states:

> "------- work on the safe limits of Aroclor vapour concentration in air is being carried on by the Medical Department at the Kettering Laboratories in Cincinnati. This work on animals is well under way, and will help us to know a little better just what is the safe limit of Aroclor Vapours that one might work in."

A question has been asked about the possible harm to plants if Ar containing paints are used in greenhouses. The reply is that most paints are somewhat harmful, and there is no evidence that Aroclo make them worse. Aroclors have been used as rabbit repellants, wi out doing any harm to vegetation.

Care is needed in laboratories etc. where Aroclors are used in heating baths; there should be very positive ventilation.

The vapours of hot Aroclors are distinctly irritating to eyes and nose above a concentration of about 3 mg per cbm in air. Newport plant report for December 1951 records burns by hot Aroclor -- a case of a splash into a man's eye -- without serious damage.

Packages of Aroclors leaving the Krummrich plant bear a label call attention to possible toxic effects.

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XI. HAZARDS, contd.

Fire Hazards

Diphenyl, of course, will burn, and reasonable care is needed in handling it. Precautions with toluene are mentioned also on page VI-29, and under "Special Risks", below.

The Aroclors are handled as if non-inflammable. Drums of materia are melted in the middle of the operating building, by open gas flames, and open gas flames are freely used to heat pipe lines.

An instruction, dated April 28, 1948, calls for a daily inspectio of safety showers, fire extinguishers and gas masks, a check list being provided.

Flanged joints on Aroclor heating system can be a source of fume. See the notes on gaskets, page 2, Section XII, below.

Phosgene may be generated in electrical flashes and fires in trans formers containing Aroclors, but this is not thought to be a major risk.

Safety Equipment

Each operator in the Krummrich Aroclor plant is supplied with gogg rubber covered gloves, canvas gloves, rubber shoes and fume respira See also page XI-1. A spare suit of clothes is kept in a case in t department. The department has the usual first aid cabinet, gas ma (chlorine), fire extinguisher, (toluene, diphenyl), stretcher, safe showers, drinking fountain, eye bath.

Special Risks

The usual care is necessary in dealing with chlorine, in lighting the gas furnaces, and in handling hot materials, steam lines etc. Diphenyl might start to burn in chlorine gas if conditions in the chlorinator were badly out of line.

A Davis "Vapotester", model M-1, Type A, (Division of Davis Emergen Equipment Co., Inc., Newark, N.J.) is held in the department for us in testing the air of the working building after toluene has been used, and for testing vessels before men are permitted to enter, an before "flame certificates" are given. The instrument contains a

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XI. HAZARDS, contd.

Special Risks, contd.

catalytic cell electrically heated to a fixed temperature, and th air to be tested is aspirated through it by means of a "squeeze ball". If combustible vapours are present, the temperature of th cell rises, and the indicating thermocouple registers on a calibrated scale.

The instrument has a zero adjustment, and it is checked twice a month by the instrument department. Flame certificates must give the number of the Vapotester used, also the data of its last calibration by the instrument department. The instrument has been useful in detecting gas escapes, and in tracing spills of gasoline, etc., from a neighbouring oil refinery into a public sewer which runs under Monsanto territory.

Mr. Benignus, of St. Louis, September 1953, discussed the dangers of using Aroclors in indoor paints. He discounted the possible dangers from phosgene formed by flash discharges in transformers charged with Aroclors.

See the references to safe handling of glycidyl phenyl ether on pages IX-161 etc.

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