

PROCESS FOR THE MANUFACTURE OF

DIPHENYL & SANTOWAX

Compiled by E. Mather, November 1950

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OUTLINE OF PROCESS AS WORKED AT ANNISTON, 1950

Benzene vapour is passed continuously through molten lead at a high temperature, causing some 16% to 20% of the benzene to be converted, in a single pass through 3 lead baths in series, into a mixture of diphenyl, terphenyl, etc, with the evolution of hydrogen. The resulting mixture of hydrogen with the reaction products and the unchanged benzene is passed up a fractionating column, which has a condenser and reflux split box, so that the sensible heat of the vapours is used to give a rough separation of the organic components of the mixture.

The fractionation system yields a forward flow of liquid benzene, and an underflow of a mixture of benzene, diphenyl, terphenyl, etc., while the hydrogen passes forward, saturated with benzene. This hydrogen stream is cooled and compressed for the recovery of more benzene. The column underflow is fractionally distilled batchwise at atmospheric pressure to yield distillates of benzene and of saleable diphenyl, and of course, intermediate fractions which are recycled to the still.

The still bottoms, containing the higher boiling components of the mixture, are called crude Santowax.

Some of the crude Santowax is distilled "straight-over", under vacuum, to yield Santowax R, and some is put to permanent storage because the supply exceeds the demand.

Crude Santowax has also been distilled under vacuum, with fractionation, giving ortho terphenyl of about 94% purity. Centrifuging of the distillate, or better, fractional distillation, gives a better product.

The m-p fraction from distillation, has been allowed to crystallize in pans, slurried with water at about 85°C, centrifuged and washed in the centrifuge with hot water. The centrifuge cake is then about 95% para terphenyl. The oil from the centrifuge liquors, separated and dried, is called "Santowax M".

See Anniston report #1924, Jan.8/45.

See page 50 below for a note on the flaking of Santowaxes.

All the recovered benzene is recycled and there is a practically continuous make-up of fresh material. This is believed to ensure the presence of a certain catalyst which is present in the raw benzene, but eliminated by the processing. (See under "Comments on Process", page 111 below).

NOTE ON CHOICE OF PROCESS

See the Anniston Report 1640, Oct.15/41, F.E.Hubbard, also Mr. A. M. Ellenburg's letter of April 28/49, citing B.I.O.S. etc. reports on the "tube" process.

The research departments at Rubon and Anniston agree in believing the tube process may be superior to the lead pot process. Some pilot plant work has been done in this direction at Anniston.

See page 116 below for the choice of the method of recovering benzene from the offgas.

SAFETY CONSIDERATIONS

(From Anniston report 1642 of October 1941, section "Health & Fire Hazards," and from discussions at Anniston in 1947 and 1950).

Health

It is obviously advisable for the operators to minimise their contact with benzene vapours and with the vapour from the hot lead, but there is no history of trouble from either of these in the Diphenyl plant. We are warned that lead vapours may be evolved during the burning out of lead traps and carbon traps.

When lower grade benzene was used for making diphenyl in 1930-31, the operators in the Arcolor department suffered from skin eruptions (acne), thought possibly to be due to chlorine derivatives from styrene in the diphenyl. The disappearance of the trouble coincided with the change to better benzene. For a time the Arcolor operators had to bathe on leaving work and a change of work clothing was provided, but this practice was discontinued.

See notes on pages 20 & 82 below relating to the general ventilation of the building.

Fire

The conversion units contain hydrogen and organic vapours at high pressures and temperatures so any failure of gaskets or of the units themselves may lead to the escape of a cloud of inflammable vapour, near to the pot furnaces. The amount of organic material present in the conversion unit at any one moment is, however, quite small, and the flow of benzene to the units can be shut off from outside the building.

In the early days at Anniston, fires were not infrequent, but there has been none of consequence in recent years. Emphasis is laid on good workmanship in the construction and maintenance of the units.

There were twelve conversion units at Anniston in November 1950, with their columns and other auxiliary equipment, two of the units being in one room, four in another, and six in a third room. The three rooms are separated by fire walls with communicating doors, some of them automatically closing, but held open by chains having a fusible link. There are two

St. Louis

February 27, 1938

Mr. T. K. Smith, Jr.

St. Louis

Agreement signed by Mr. R. E. Cole, Jr.
Approved by the surgeon general 10/16/37

AGREEMENT BETWEEN THE U. S. PUBLIC HEALTH
SERVICE & THE MANUFACTURERS OF CHLORINATED
NAPHTHALENES, CHLORINATED DIPHENYLS AND
CHLORINATED DIPHENYL OXIDES

You asked about the second item in this signed agreement which
we quote as follows:

"As further evidence of cooperation, the manufacturer agrees
to insert on all bills of sale the following notation:

"This product is sold under direct agreement with the
U. S. Public Health Service and if re-sold as such or
in mixtures thereof for further fabrication within
the United States, it is necessary that such products
be labelled by you as follows:

"This package contains (Name of Product)

AVOID REPEATED CONTACT WITH THE SKIN AND
INHALATION OF THE FUMES AND DUSTS."

Attached is original and duplicate invoice blank showing that our
bills of sale do not carry the notation as given in the second part
of the agreement noted above. It would be most difficult to under-
stand how any of our direct customers could comply with this
agreement, and to cite one example, we mention Plastics Film
Corporation. Here Aroclor 1254 is used as one of the component
plasticizers in the film which Plastics Film Corporation then
sell to various fabricators for fabrication. This, of course,
represents resale of Aroclors in mixture with other ingredients
in vinyl, and would appear to come under the letter of the agree-
ment. However, as a result of this transaction Plastics Film
Corporation would not be interested in stamping their vinyl film
with our Aroclor warning label.

The wording of our Aroclor label about handling is relatively
mild, yet, in a few instances we know that people not familiar
with chemical products have mis-interpreted it to an unjustifiable
extent. On the other hand, in the very few instances where misuse
of Aroclor (especially at elevated temperatures) has led to law
suits, it was highly desirable and protective to us in having
our current label on the Aroclor packages.

MONS 094551



Since the wording of the label was formulated and put into use, skin patch tests run under competent medical supervision indicated that Arcolors are neither skin irritants nor skin sensitizers. This is indicated in our literature, but of course is not intended to mean that people should bathe in Arcolor. There are instances in the commercial use of Arcolor where people have immersed their arms up to the elbow, day in and day out, in the liquid Arcolors, and of course we do not approve of this, and to avoid such misuse of Arcolor, the wording on our label to avoid repeated contact with the skin seems highly significant. Back in 1938 or thereabouts, when the Arcolor applications were relatively few and the customers about equally few, there was indeed the prize application of using Arcolor 1254 as a chewing gum plasticizer. The wording of our label would not be compatible with this sort of thing.

Since so many of the new Arcolor applications involve their use at elevated temperatures, the wording of the warning label to avoid inhalation of fumes is especially significant. We constantly keep this factor in mind in our development work, and emphasize it in direct contacts as well as indirect contacts such as our literature. While the toxicity hazard of Arcolor's fumes is well established and should be thoroughly understood by all, yet, as we go along we find that we are always confronted with violations in one degree or another, and indeed, regard keeping in touch with these things to be a major responsibility in the promotion of Arcolors.

Strictly speaking, the matter of inhaling Arcolor dusts might be deleted from the warning label, as surely most of the commonly used Arcolors certainly are not dusty, and the powdered materials such as Arcolor 1268 and 1270 and 1271 are reported in the literature as being of a relatively low order of toxicity. This item on dust may apply in the case of unloading a drum of Arcolor 5460.

Referring to the few deaths, and the relatively large number of acne or dermatitis cases arising during the war, in connection with fabricators of Navy cable coating materials using a mixture of Arcolor 4465 and Halovax, there are two things to keep in mind. One is that this combination of chlorinated hydrocarbons is more toxic than the chlorinated biphenyl or terphenyls alone; and secondly, in this program of operations, proper working facilities and cleanliness were overlooked. In fact, the workers' wives at home even acquired acne and dermatitis which was traced back to the halogenated hydrocarbon compounds.

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In the light of the immediate above, it is interesting to keep in mind that we are currently selling at least two and one-half million pounds a year of, particularly, Arcolor 5460; but also some Arcolor 4465 for hot melt impregnation of asbestos wound wire, and also as impregnating agents used in the construction of Navy cable.

In the past, when the toxicology of Arcolors may not have been particularly well understood, this factor was certainly a heavy load on the development of these products. The subject remains not the easiest one in the world to understand, but in view of the large stake that we now have in the rather widespread commercial use of Arcolors, we constantly strive to learn more about this subject of Arcolor toxicology and to safeguard against any possible hazards.

P. G. Benignus

RM
Att.

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