3. It has been observed that fine particles may have their solubility diminished by an electrical charge or adsorption effect on the surface.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE]

THE PREPARATION OF DIPHENYL

BY CARROLL H. LOWE AND C. JAMES

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After the publication of a paper[1] in which the preparation of diphenyl was given, one of the present authors received several letters stating that the process failed to give good results. Since these statements were so contrary to those given in the original article, it seemed advisable to make a reinvestigation. A careful study of the faults of the first method revealed the fact that there were two striking difficulties which could be overcome only by bringing much sounder mechanical principles into play.

The first troublesome factor was the incessant short circuiting due to the expansion and sagging of the Nichrome ribbon filament, when heated. The second element of trouble was that due to superheating at the points where the filament came in contact with the means of support.

Description of the New Apparatus

As in the old, the new apparatus consisted of a 12-liter Pyrex flask, supported by a tripod. In the neck of the flask a tightly fitting stopper was inserted, through which a hole had been bored for the delivery tube of the inverted condenser. The latter was retained in a perpendicular position by means of an iron stand and clamp. In addition to the hole for the delivery tube, three symmetrically placed, very small holes were bored, through which passed the rods of the internal mechanism. Their purpose was to serve as threaded axes of the necessary binding posts for the essential electrical connections.

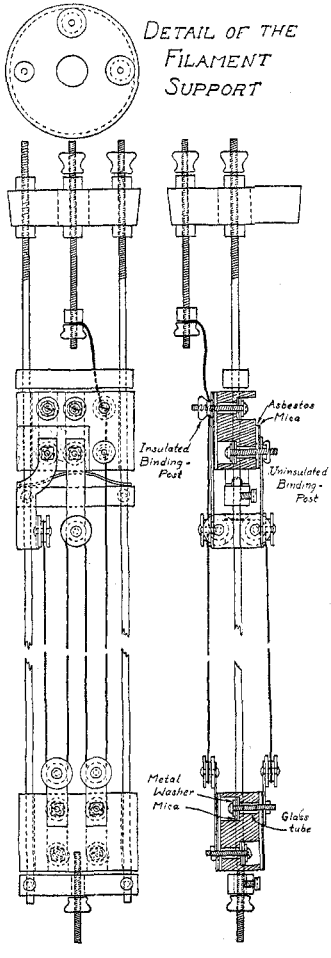
As has been previously mentioned, the problem was mainly one concerning an adequate filament support. After considerable experimentation, a type that was highly satisfactory was devised, all the faults of the old process being completely eliminated. The main supports consisted of two parallel steel rods, threaded on the ends that passed through the cork. These were securely retained in position by three steel cross-braces, two of which were held firmly in place by set screws.

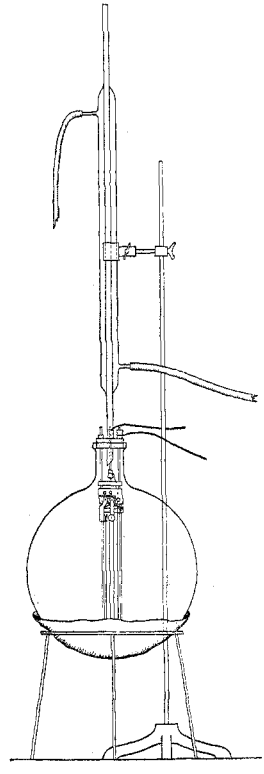
Two larger blocks of steel were grooved on the edges and placed between the rods. This allowed the former to slide up and down, easily, as far as the cross-braces would permit. Between the middle cross-brace and upper block a powerful, arched strap spring of steel was inserted.

[1] THIS JOURNAL, **39**, 933 (1917).

Through the center of the lower cross-brace, a 6mm. hole was bored. This allowed free passage of the threaded steel wire which was screwed into the lower block, parallel to the main supporting rods.

On the opposite end of the threaded wire was an adjusting screw, the purpose of which was to secure the desired tension on the filament before





ASSEMBLED APPARATUS

use. Once the filament was in position, it became an easy matter to tighten it, and the resulting tension would cause a depression of the arched spring. Upon passage of the electric current through the filament the expansion which took place was taken up by the tendency of the depressed spring to assume its former position, thus keeping the filament taut at all times. This removed the possibility of short circuiting and eliminated one of the main difficulties of the old apparatus.

Instead of using a 4-stranded filament as formerly recommended, one of 8 strands was used, thereby doubling the heating surface. This filament did not reach a higher point than the base of the neck of the flask.

On each of the movable blocks were brass, flanged discs over which the filament passed from strand to strand. This method of holding the filament in place did away with the troublesome superheating and prevented any danger of breaking due to sharp cornered hooks.

One of the special features in this apparatus is the method of insulating the flanged discs against contact with the blocks themselves. The details of this, however, are much better given by the accompanying drawings than could be attempted in words. Whatever specifications are lacking above will be found clearly indicated in these drawings.

Precautions

In attempting to run this new process a few precautions are absolutely necessary.

To begin with, the operator must never lose sight of the fact that it is a very dangerous procedure to attempt heating the filament, to incandescence, until all of the air within the flask has been expelled. Should any oxygen be present, it will promote combustion of the benzene and a very serious explosion may result. As a measure of additional safety, it is highly advisable to install an automatic cut-off, in case the current is temporarily shut off.

Care must be taken not to over-heat the filament; it should be maintained at a yellowish-red tinge. Under the best conditions a mist forms, the benzene returning from the condenser has a yellowish color and diphenyl streams down the sides of the hot flask. Formation of carbon at different points will give a warning of over-heating. It should be remembered that no part of the filament ought to be in the liquid phase. If the bottom of the lower block just touches the surface of the liquid, sufficient heat will be transmitted through it to keep the liquid boiling.

It is highly advisable to keep the filament at an even temperature throughout the entire run, although it will not break should it be cooled a few times. It is only a matter of 5 or 10 minutes' time to replace the old with a new filament.

The mechanical parts should be cleaned often in order that the tarry residue, which is deposited all over the surfaces, may be prevented from retarding their free and easy motion. When the filament support is not in use, it should be kept immersed in a small covered container filled with benzene.

Results.—One kilogram of diphenyl has been obtained in a 24-hour run, using a current of 110 volts and 10 to 12 amperes. The amount of by-products separated by fractional distillation is not very great.

The application of this type of apparatus for other processes, involving simple heat effect, or where the filament is covered with catalytic material such as oxides, etc., is now under investigation.

Summary

1. A filament support has been described which eliminates all previous difficulties in the preparation of diphenyl, such as local heating and short circuiting due to expansion and sagging.

2. Very good yields of diphenyl can be obtained from benzene by maintaining the Nichrome filament at a yellowish-red heat.

3. The benzene used was commercially pure and not anhydrous. The addition of more water did not hasten the reaction.

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[CONTRIBUTION FROM THE SOILS LABORATORY, AGRICULTURAL EXPERIMENT STATION, UNIVERSITY OF MISSOURI]

THE NATURE OF THE ACIDITY OF THE COLLOIDAL CLAY OF ACID SOILS

BY RICHARD BRADFIELD

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The problem of soil acidity has probably been investigated more than any other one soil problem, but in spite of the vast amount of work that has been done there is still considerable doubt as to its real nature.

Fisher[1] in his excellent résumé of the subject concludes: "It cannot be said that the enormous amount of work done has either solved the practical problem or clarified our ideas as to what exactly soil acidity means."

The earlier chemists believed with Sprengel[2] that soil acidity was due to the accumulation of complex insoluble organic acids. Recent work by Odén,[3] using electrochemical methods, has established the validity of Sprengel's contention when applied to soils high in organic matter. Some of our most acid soils, however, are very low in organic matter and their acidity must be due to some other cause. If aqueous extracts of most acid soils are boiled to expel the carbon dioxide they will not as a rule be sufficiently acid to redden litmus paper even though the moist soil itself may change it almost immediately. This and similar observations led to some doubt as to the existence of real acids in soils and to the idea of "negative acidity." The conception of "negative acidity" had its origin in the work of Van Bemmelen who found that certain colloids and soils exhibited a preferential absorption for bases when treated with neutral salts, leaving the solution acid. This idea was developed into the selective adsorption theory of soil acidity by Cameron, Parker, Harris and others.[4] Ramman discarded the expression

[1] Fisher, *J. Agr. Sci.*, **11**, 20 (1921).

[2] Sprengel, *Archiv. Ges. Naturl.*, **8**, 145 (1826).

[3] Odén, *Trans. Faraday Soc.*, [2] **17**, 288 (1922).

[4] Cameron, *J. Phys. Chem.*, **14**, 320, 393 (1919). Parker, *J. Agr. Res.*, **1**, 179 (1913). Harris, *Mich. Expt. Sta. Tech. Bull.*, **19** (1914). Ramman, "Bodenkunde," J. Springer, Berlin, **1911**.