

ROLE OF THE ORGANIC EXPANDER IN MODERN LEAD/ACID BATTERIES

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Introduction

Lead/acid batteries to-day could be considered to be the same batteries with negative and positive plates as they were some 60 to 70 years ago. While the principle is the same, however, beneath the cover much has been improved. The modern battery weighs only one quarter of the old version (for the same capacity), has a life time two to three times longer, is much more reliable, and has many other practical advantages. Indeed, car owners may now forget there is a battery in the car, its performance is so advanced.

A great deal of research work gave rise to all these improvements and innovations. Nevertheless, a small part of a battery, at least in weight terms (*i.e.*, a few grams in a car battery), the organic expander — unknown to most battery users — has played a significant role and has an important task in the battery.

Already, by the second and third decades of this century, a correlation between sawdust in the negative paste and improvement in the cold-start capacity had been discovered. Systematic research soon unveiled the components of the sawdust that caused this beneficial change. The remainder of the story is mainly chemistry. However, a major part of the present knowledge of the role of the organic expander is empirical; there are still many unanswered questions.

The development from sawdust to the modern, highly effective, organic expander is partly the fruit of open and honest co-operation between battery researchers and chemical suppliers. When the history of expander development is traced, it becomes clear how the expander effect was discovered.

Expander development

The first milestone was to discover the beneficial presence of wood in a battery. The second step was to determine which component of the wood exerted the positive influence. Without doubt this was the lignin. The fibre, the other half of the wood, was found to be inert and therefore was abandoned. The subsequent stages of the development history were the repeated testing of the lignin and lignin derivatives, the correlation analysis between

lignin and lignite modifications, and the following vital parameters of the battery: (i) cold-start capacity; (ii) charge acceptance; (iii) service life.

It was observed that the action of the organic expander altered during the lifetime of the battery; investigations were conducted under rapid and extreme charge/discharge cycling. It soon became obvious that increased amounts of the organic expander improved the cold-start capacity, but adversely influenced the charge acceptance. Therefore, it was necessary to find a compromise between these two important performance parameters. It became equally clear that the other components of the expander — the carbon black and the barium sulphate — played only a secondary role. Therefore, further research was concentrated on the lignin/lignite component. It was subsequently discovered that the required expander action depended on the chemical structure, the chemical stability, the dispersing power, and several other characteristics of the lignin/lignite compound.

Since it was both technologically and chemically easier to control lignin derivatives rather than lignite to give a uniform product, the lignin soon assumed the leading role in the application of organic expanders. The following part of the development history, therefore, will be concentrated on the role of lignin.

Lignin structure

Wood consists, mainly, of three types of chemical compound: cellulose, hemi-cellulose, lignin. Whereas the chemical structures of cellulose and hemi-cellulose are known, that of lignin has still to be resolved. However, it has been determined that lignin is a polymer containing phenylpropane units (Fig. 1). These units form a three-dimensional network structure which chemically binds together the cellulose and other carbohydrates. A great many details on how the phenylpropane units are joined together, as well as on the structure of certain fractions of the lignin, have been agreed. Scientists differ, however, when it comes to the nature of the total structure of the lignin molecule.

During the past two decades, many different models have been proposed for the basic structure of the lignin molecule. More and more evidence supports the Freudenberg formula (Fig. 2) that was advanced in 1964. Freudenberg stated: 'There is no doubt, that neither spruce lignin, nor any other kind of lignin will ever be satisfactorily depicted by a single formula, even by a very extended one'. It is important to keep in mind that the term

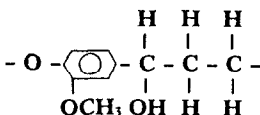


Fig. 1. Phenylpropane groups in lignin.

'lignin' refers to a mixture of substances of similar chemical composition, but having structural differences.

Lignin in its natural form is insoluble in neutral liquids and organic solvents. A common method of separating lignin and other compounds is to digest wood chips in a hot, aqueous acid solution of calcium bisulphite. During this process, part of the lignin is sulphonated according to the simplified reaction shown in Fig. 3. In addition, some of the linkages in the lignin network structure and lignin carbohydrate attachment are hydrolyzed, as shown in Fig. 4.

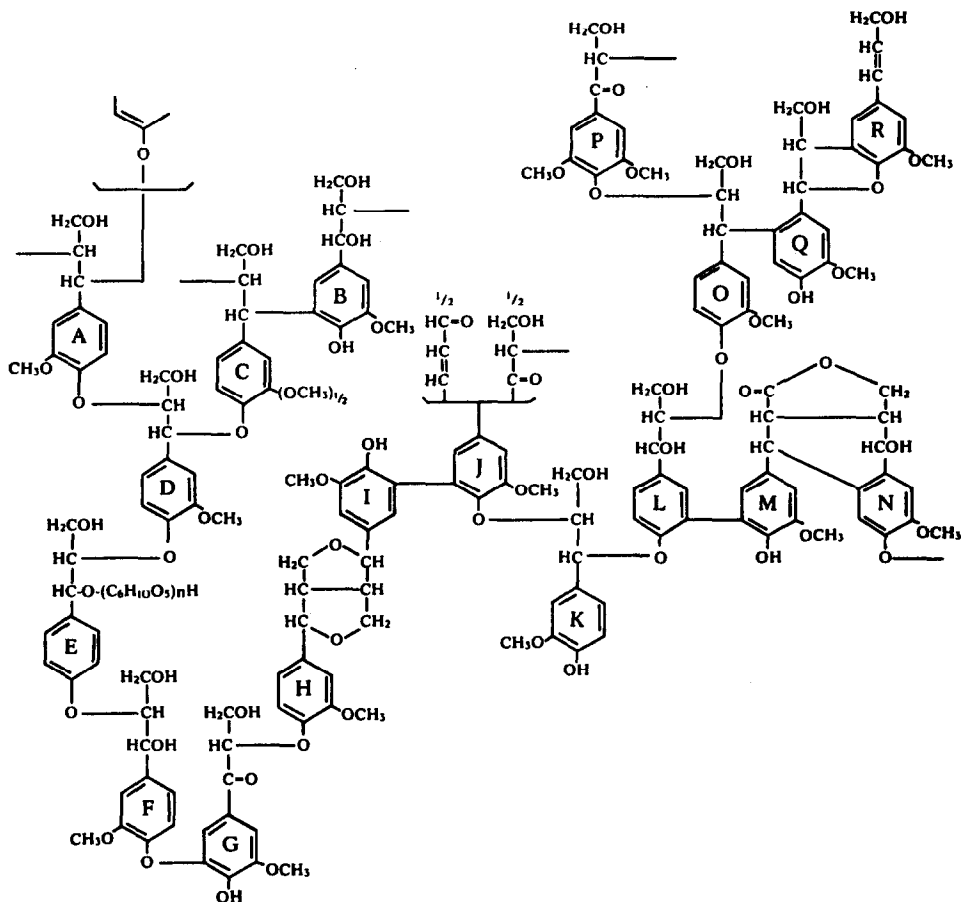


Fig. 2. Freudentberg formula for lignin.

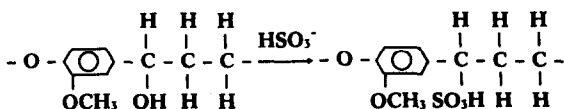


Fig. 3. Sulphonation of lignin.

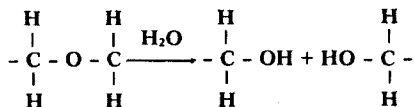


Fig. 4. Hydrolysis of lignin.

Expander performance

Variations in the expander effect posed the greatest problem to battery manufacturers. Thus, constant quality parameters were requested. This also increased the activity towards standardizing directions in the research work.

Of the available lignin sources, the sulphonated lignin from the pulp production process proved to give the most constant and reliable quality, and became the basis for further development. After the sodium salt of ligno-sulphonic acid had become commonly accepted as an organic expander, improvements were achieved by selecting slow-growing Norwegian spruce (*Picea abies norvegica*) as optimal raw material. Later, the stability of the lignin in sulphuric acid, the dispersing properties, and the inhibiting influence on crystallization of the lignin compound, were improved. The improvements were achieved by determining the optimal degree of desulphonation, depolymerization, and demethoxylation.

The above process is linked to the vanillin oxidation process that causes a material reduction in the organically bound sulphur content, as well as condensation, cleavage, and rearrangement reactions due to oxidation and hydrolysis. These strictly controlled reactions increase the number of phenolic and hydroxyl groups in the molecular structure, which improve the formation as well as the initial performance of battery plates. The oxidation and hydrolytic cleavage also form degradation products that have a favourable effect upon the capacity of storage batteries during repeated charging/discharging.

During the lignin expander manufacturing process, extreme care is taken to concentrate the organically active substances and to keep adverse impurities (mainly heavy metal contamination) to the lowest possible level.

Normally, the cold-start capacity of automotive batteries is the parameter that manufacturers are mainly interested in increasing to a maximum with the help of the organic expander. The standard test method in most European countries is the simulation of a severe winter start of a car. The battery is cooled down to $-18\text{ }^{\circ}\text{C}$, discharged at five times the nominal capacity, and the time for the voltage to fall to 1 V per cell is measured. This procedure is repeated for several charging/discharging cycles and the results are plotted graphically (e.g., Fig. 5).

Until refined and purified sodium lignosulphonates were developed, lignite was also commonly applied as an organic expander. Lignite is well known as a brown pigment and is called 'van Dyke brown' in English or 'Kasseler braun' in German. The principal difference between the effect of lignin and lignite expanders is the immediate improvement in cold-start

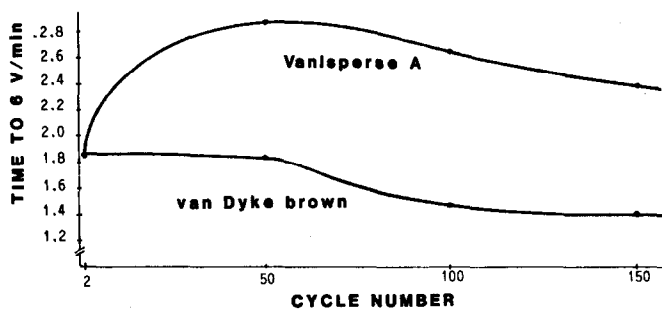


Fig. 5. Cold-start performance of batteries (60 A h capacity) at 300 A and -18°C : effect of negative-plate expander.

capacity with the lignin. On the other hand, lignite gives an initial constant, but later slowly decreasing, effect (Fig. 5).

To achieve the improved cold-start capacity of a battery, the expander must also increase the relative surface area of the negative paste. The enhanced surface also shows a strong tendency to enter into oxidative reaction with atmospheric oxygen, especially under the conditions of a special drying procedure, employing a kerosene bath, which may cause a fire hazard. The application of inert gas is the safest method of reducing oxidation.

The important benefits of the lignin expander result from adsorption (or plating-out) on the lead particles during charge, which prevents lead sulphate from precipitating on the lead particles during discharge. In the absence of an efficient expander, lead sulphate deposits as a closely adhering, impervious layer that markedly limits the plate capacity. The presence of the lignin, however, renders the lead sulphate film porous. It may be said that the increased capacity and the reduced polarization are both due to a controlled improvement in the structure of the lead sulphate film.

Excessive addition of organic expander can result in adverse effects. As mentioned above, too much expander may cause a decrease in the charge acceptance. According to the literature, this phenomenon can be compensated to a certain extent by adding a nickel compound.

VANISPERSE A is the trade name of a well-known and world-wide applied organic expander manufactured by the author's company. This sodium lignosulphonate is produced exclusively from Norwegian spruce by a rigidly controlled chemical process. Today's VANISPERSE A is the result of more than twenty years of continuous improvement, a tremendous research effort, and a great deal of close co-operation and discussion with the leading battery manufacturers of Europe.

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