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UNITED STATES PATENT OFFICE.

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HAIR AND FUR DYE.

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To all whom it may concern:

Be it known that we, WOLF KRITCHEVSKY and WILLIAM K. NELSON, both citizens of the United States, residing at Chicago, in the county of Cook and State of Illinois, have invented a certain new and Improved Hair and Fur Dye, of which the following is a specification.

Our invention relates to the artificial coloring of hair, and particularly to a novel dye.

Hair dyes have been used since early in the history of civilization. In earlier times the substances generally employed for this purpose consisted of the salts of metals, such as lead, copper, silver and iron; also vegetable extracts, such as that of henna, reng and nuts of various kinds containing gallic and pyrogallic acids.

In modern times, the more popular hair dyes were composed of para or ortho diamines, amino phenols or naphthols and trihydroxy derivatives of benzene, as well as of diamido phenols. The satisfactory results obtained by the use of these organic dyes are explained by the fact that each has the inherent property of oxidizing when exposed to the air or to the action of oxidizing agents. In the process of oxidation of these compounds, new chemical compounds result which are highly colored and insoluble in water, and when deposited on the hair, they impart thereto the desired color.

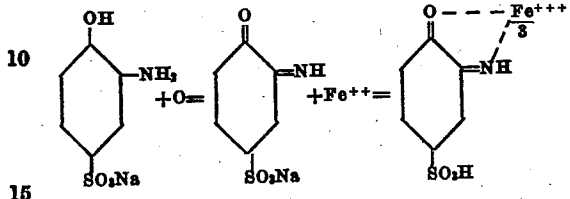
Hair dyes prepared from the specified compounds leave little to be desired from the tinctorial point of view, but they are highly poisonous and are likely to cause serious harm to the users. This is now well known and the effects are described in the work by Erdman and Tomashevsky (Munch. Med. Woch. 1906).

Much experimentation has been carried on with the idea of eliminating the toxicity from the described compounds. In that connection, a rule is given in the book by Dr. S. Frankel, entitled "Arzneimittel Synthese". He states that cyclic hydrocarbons, amines or phenols, which are known to be poisonous, lose partially or completely their toxicity after replacing one of their hydrogen atoms with a group of an acid character. As an instance aniline is cited, which is poisonous, while sulphanilic acid and anthranilic acid are perfectly harmless. This principle was applied by Dr. Erdman as a basis for a series of hair dyes consisting of the sodium salts of aminophenolsulphonic acid, of aminodiphenylaminesulphonic acid etc. These dyes have had very limited success, for the particular reason that the shades obtained by their use are not natural; further, the acid group introduced into the compounds weakens their tinctorial strength. Still another objection is that the final products of oxidation are generally of a soluble nature and are easily washed out.

Our discovery is that by obtaining, at a certain stage, the metallic salts, the tinctorial value is greatly increased, and dark shades having a natural appearance are obtained, and are fast relative to light and water. The results obtained by us are in accord with the theory of mordants and of the formation of lakes from dyes combined with certain mineral salts.

When a sulphonic or carboxylic acid of an aminophenol or of an aminonaphthol and their derivatives, as amino and arylamino, of a diamine and its derivatives, as amino and arylamino or of a polyphenol, or their respective sodium salts, is combined in solution with a salt of a metal such as iron, copper or chromium, or any other substance having mordanting properties, no change in the molecular structure of the organic radical takes place unless there is an oxidizing agent present. Whether it is by means of the oxygen from the air or by the use of various oxidizing materials, as soon as oxidation sets in, the change of the organic radical into a chinone structure begins. This changed form when combined with the metallic salt results in a highly colored insoluble compound.

As an illustration, we will take a solution consisting of orthoamidophenolsodium sulphonate and iron sulphate. In the presence of an oxidizing agent the change in the structure of the organic radical and the formation of the iron salt of the chinone sulphonic acid proceeds very rapidly, thus:



It will be seen that the iron in this reaction becomes oxidized to the trivalent variety. This highly colored insoluble compound fixes itself to the hair, imparting to it a dark shade of natural appearance. The fact that the dye is mordanted makes it fast to light and water.

We have observed, in our work, that in the case of the metallic salts which possess a lower and a higher state of oxidation, such as in the case of iron and copper, the oxidation of the organic radical proceeds at a much faster rate and more completely than in the case of where metals having only one state of oxidation are used. The reason for this can be ascribed to the fact that metallic salts having a capability of forming higher stages of oxidation are usually much more oxidizable than the organic radicals. They thus act as oxygen carriers by first assuming a higher state of oxidation and then acting on the organic radical as an oxidizing agent. Meanwhile, they are being reduced in this manner to the lower state, and the process is repeated until complete oxidation of the organic radical and the metallic combination of the chinone acid takes place.

In preparing the solution of our dye, care must be exercised to have the proper hydrogen ion concentration. If the solution is too alkaline, premature oxidation takes place, as well as precipitation of the metallic salt. If, on the other hand, the solution is too much acid, there is a tendency for the organic acid radical to precipitate out. We have found that a very slight alkaline reaction on turmeric test paper is the right point of hydrogen ion concentration in our solution.

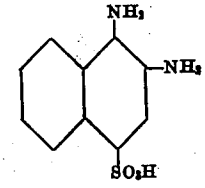
As alkali reagents in which to dissolve our organic acid, we may use carbonates, hydroxides, ammonia, borates, borax, phosphates, soluble salts of amino acids, acetates or sulphites.

As acidifying reagents, we may use organic acids and acid salts such as citric acid, formic acid, acid tartrate, acid sulphite like sodium bisulphite, acid sulphate like nitre cake.

The following examples illustrate the preparation of the product:

I.

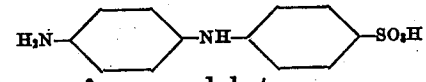
30 gms. 1:2 naphthalenediamino-4-sulphonic acid



10 gms. potassium hydroxide.
5 gms. potassium bichromate.
Water to make one litre.

II.

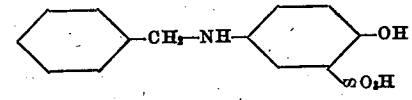
20 gms. 4, 4′ amidodiphenylaminesulphonic acid



10 gms. ferrous sulphate.
20 gms. borax.
5 gms. sodium hydrogen sulphate.
Water to make one litre.

III.

40 gms. monobenzylparaamidophenolsulphonic acid



60 gms. sodium sulphite.
10 gms. manganous sulphate.
15 gms. sodium hydrogen sulphite.
Water sufficient to make one litre.

The above quantities may be varied within reasonable limits and we anticipate making various combinations of this class of compounds for the purpose of obtaining various shades.

The method of application of our preparation is by brushing the same on the hair with a small brush and subsequent exposure to the action of the oxygen in the air; or, to an electric drying appliance; or by mixing the hair dye immediately before use with hydrogen peroxide or other reagents capable of giving off hydrogen peroxide or oxygen; or by treating the hair after or before the dye was brushed on with hydrogen peroxide or other oxidizing agents.

We claim:

1. A hair dye in the form of a colorless aqueous solution, consisting of the reaction products of an organic cyclic compound belonging to the aromatic series of the general formula



in which C stands for an aromatic cyclic hydrocarbon and its homologues, in which R stands for an hydroxyl group, or an amino group and its substitution products, the position of the radicals to each other being such as to be capable of forming a quinoidal structure, in which AC stands for an acid grouping, the position of the acidic group to the other radicals being immaterial; together with a metallic salt capable of acting as a mordant, an alkaline reacting substance to dissolve the organic acid and form a salt, and an acid reacting substance to neutralize the excess alkalinity, so that the solution is substantially neutral.

2. A hair dye consisting of a water solution of 1:2 naphthalenediamine-4-sulphonic acid, ferrous sulphate, borax and sodium acid sulphate.

Signed at Chicago, Ill., this 15th day of December, 1924.

WOLF KRITCHEVSKY.
WILLIAM K. NELSON.