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PIGMENTS GROUP RESEARCH REPORT

LIGHTFAST AZO - PIGMENT COMPLEXES

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JACKSON LABORATORY

PIGMENTS GROUP RESEARCH REPORT

LIGHTFAST AZO - PIGMENT COMPLEXES

JUNE 4, 1951 to MAY 1, 1952.

CHARGE: A-II-268

SUBMITTED BY: A. D. REIDINGER A. D. Reidinger DATE SUBMITTED: 3/20/53

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INTRODUCTION:

The unusually good lightfastness of Green-Gold, YT-562-D, (Ni complex of parachloraniline coupled to 2,4-dihydroxy quinoline) has led to the search for other metallized azo pigments of similar properties. A great number of combinations were prepared and examined by Jackson Laboratory but a review of this work did not disclose any products which possessed both the relatively good color value and lightfastness of YT-562-D. The object of the present investigation was the preparation and evaluation of metal complexes, derived from coupling components which were analogous to 2,4-dihydroxy quinoline in having a β diketo structure or the corresponding enolic form.

SUMMARY AND CONCLUSIONS:

A number of coupling components possessing some of the structural characteristics of 2,4-dihydroxy quinoline were prepared or obtained from other sources and when possible were coupled to common diazo components and converted to their nickel or copper complexes. None of the metallic derivatives obtained showed any advantage over Green-Gold, YT-562-D, and many of them were inferior in respect wither to tinctorial properties or lightfastness.

It was not found possible to form metal chelates of azo dyestuffs in which the diazo components were devoid of acidic groups and the second components were acyclic compounds such as acetyl acetone or in which the active methylene group was part of a straight chain as in acetoacetanilide. This was also the case with the homologous components - benzoyl acetone and benzoyl acetanilide. Similar inability to metallize was observed on the part of the coupled products from 2-acetonyl benzaminazole and 2-acetonyl benzthiazole. 2-phenacyl benzaminazole coupled with difficulty and the product metallized slowly and incompletely.

In contrast, analogs of 2,4-dihydroxy quinoline, such as 2,4-dihydroxy-N-methyl quinoline, 4-hydroxy-2-methyl quinoline, and benzotetronic acid (the oxygen analog of DHQ), when coupled to diazotized parachloraniline, gave dyestuffs which combined readily with nickel. Of these only the O analog approached YT-562-D in shade and lightfastness and it was considerably weaker and duller. The other products were browns of poor lightfastness and bleed resistance. 2-hydroxy-4-methyl quinoline could not be coupled under the usual conditions due to the relatively inactive - CH_2 - group.

Two isomers of dihydroxy quinoline - 1,3 and 1,4-isoquinolinediol - also gave less satisfactory results than 2,4-DHQ. The former, coupled to aniline and parachloraniline, did not react with nickel but formed a dull yellow copper derivative which was poor in lightfastness and bleed. When coupled to 4-chloranthranilic acid, a copper derivative (a partially complexed metal salt) was obtainable, which exhibited excellent lightfastness in full shade drawdown. However, poor bleed resistance, as well as its brownness, make it of little value. 1,4-isoquinolinediol coupled to parachloraniline gave violet nickel and copper derivatives which were too dull in shade and too poor in oil bleed to be of interest. The copper complex possessed good lightfastness in full shade drawdown.

The greater ease of metallization of many heterocyclic compounds was confirmed by results with 1-phenyl-3-methyl-5-pyrazolone and 5,5-dimethyl cyclohexanedione-1,3. In both cases nickel derivatives could be prepared, the former with both aniline and parachloraniline as diazo component giving yellows of good lightfastness in full shade but having poor lightfastness in ZnO tints. Dimethyl cyclohexanedione coupled to parachloraniline formed a brown nickel compound (97% purity). However, lightfastness and bleed resistance (in oil) were poor.

Other cyclic compounds such as 1,3 indandione and 6-ethoxy thioindoxyl gave unsatisfactory results. Both were difficult to couple. The latter, when coupled to parachloraniline did not show evidence of metallization with nickel or copper.

DISCUSSION:

An attempt was made to correlate the ratio of the enol-keto equilibrium of the various coupling components with the ability of the coupled products to metallize, using data obtained by the Kurt-Meyer bromination procedure. However, the facility with which metallization occurred did not appear to be related solely to the enolic contents thus obtained, although it may be significant that the reaction of 2,4 dihydroxy quinoline is quantitative and is used as an analytical method. Furthermore, 5,5' dimethyl cyclohexanedione-1,3, which was successfully metallized, is reported to have a high enol value. The lack of correlation in other instances may have been due to the use of alcohol as solvent in testing the components while employing water as the medium for metallization of the corresponding dyestuffs.

Replacement of water by ethyl alcohol or ethylene glycol, as thus suggested, did not give noticeably better results in instances where metallization was difficult.

In order to obtain the metal derivatives in purer form, some of them were extracted in a Sohxlet with benzene or acetone. All of those thus treated apparently contain unreacted dye or other soluble components, ranging in amounts from 4.0% extracted from a laboratory sample of Green-Gold to 27.2% extracted from the nickel derivative of parachloraniline → 5,5 dimethyl dihydro resorcin. Since this pigment was found by analysis to be 97% pure, the metal complex is evidently noticeably soluble. Actually all the extracts upon evaporation left residues which gave a strong test for nickel. Although some of the products were improved in tinctorial properties by extraction, better lightfastness and bleed resistance resulted in only a few instances.

EXPERIMENTAL DETAILS:

The following coupling components which were used were available in Jackson Laboratory files or were obtained from chemical suppliers -

Acetyl Acetone
Benzoylacetone
Dibenzoylmethane
Ethyloxal acetate
Acetoacetanilide
Benzoylacetanilide
2,4 Dihydroxy quinoline
2-Hydroxy-4-methyl quinoline
1,3 Isoquinolinediol
1-Phenyl-3-methyl-5-pyrazolone
Cyclohexanediol-1,3.
5,5' Dimethyl cyclohexanediol-1,3
1,3-Indandione
6-Ethoxy thioindoxyl

A number of intermediates were prepared by methods outlined in the literature, the details for which are to be found in N.B.1290. These included:

N-Methyl acetoacetanilide
N-Ethyl acetoacetanilide
2-Acetonyl benziminazole
2-Phenacyl benziminazole
2-Acetonyl benzthiazole
4-Hydroxy-2-methyl quinoline
2,4-Dihydroxy-N-methyl quinoline
Benzotetronic Acid
7-nitro-2,4-dihydroxy quinoline
Anilides of maleic and oxalacetic acids.

For details of couplings and metallizations see N.B.1396.