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PIGMENT COLOR RESEARCH REPORT

JACKSON LABORATORY

PIGMENTS GROUP RESEARCH REPORT

ETHYL ESTER OF 1-PHENYL-5-PYRAZOLONE-3-CARBOXYLIC ACID

Period Covered: PATENT SEARCH

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JACKSON LABORATORY

PIGMENTS GROUP RESEARCH REPORT

ETHYL ESTER OF 1-PHENYL-5-PYRAZOLONE-3-CARBOXYLIC ACID

PATENT SEARCH

SUBMITTED BY: A. D. Reidinger 7/13/48 DATE SUBMITTED 6/8/48

APPROVED BY: D. B. Killian 7/13/48 DATE ISSUED: 7/13/48

DUP050066977

SUBJECT:

1-Phenyl-5-Pyrazolone-3-Carboxylic Acid, Ethyl Ester.

HISTORICAL BACKGROUND:

This intermediate coupled to 3,3' dichlorbenzidine is a component of Vulcan Red B which has found considerable use as a rubber pigment and may also have application in some plastics. A patent, U.S. #1,977,936, issued October 23, 1934, covering water insoluble dyestuffs of this type is held by General Aniline Works, Inc. Use for coloring rubber is claimed in U.S. #2,002,174, also assigned to G.A.

Consideration has been given to the merits of pigments of the Vulcan Red type, manufacture of which would have to be licensed by the patentee. Questions were also raised on the patent status of the intermediate which is obtained by the method common for such pyrazolones, viz. condensation of phenyl hydrazine with ethyl oxal acetate (sodium salt) and ring closing in the presence of an alkali, in this instance sodium carbonate.

OBJECT OF THIS STUDY:

To determine whether the ethyl ester of 1-phenyl-5-pyrazolone-3-carboxylic acid or its process of manufacture are dominated in this country by existing patents. Also to record references to use of the intermediate in addition to those cited above.

CONCLUSIONS AND RECOMMENDATIONS:

Since no dominating patent has been found it is believed we are free to manufacture the subject intermediate. The process for preparation of this pyrazolone ester was described in its essential details as long ago as 1888 (see Ref. 14 below).

DUP050066978

SEARCHED:

Patent Literature:

Folders in J.L. Patent Library.

Heterocyclic Compounds	300, 300.2, 300.21
Compounds with 2 Nuclear N atoms	308
Organic Compounds-Esters G	00.42
Azo Dyes	640
Mono Azo Dyes	641, 641.05, 641.055, 641.1, 641.15, 641.155
Disazo Dyes	642, 642.3, 642.35
Lakes and Pigments	650, 650.4
Lakes and Azo Lakes	651, 651.4
Pigments, Organic & Azo	653, 653.1, 653.14
Disazo - Tertiary Azo Pigments	653.14,642.3
Final Color first formed on the Fiber	630, 631, 631.01, 631.012, 631.012 1, 631.111, 631.112
Chemical Processes	931.1, 931.116 12, 931.146 21, 931.141 13, 931.141 1, 931.1455

General Literature:

Beilstein Handbuch der Organische Chemie, Edition IV.
Chemical Abstracts 1927-1947
Chemische Zentralblatt 1922-1943

FOUND:

Patents:

Reference 1.	U.S.	1,766,813	
2.		1,794,218	
3.		1,819,547	(B 243,758, D 493,128)
4.		1,874,474	(F 660,576)
5.		2,012,553	(B 413,198, D 626,831, F 764,995)
6.		2,023,953	(B 428,535, D 601,717)
7.		2,028,439	
8.		2,137,498	
9.		2,228,303	(F 849,759)
10.	B.	405,003	
11.		584,255	
12.	D.	629,813	
13.	Belg.	434,679	

Literature:

Reference 14. Wislicenus, Annalen 246, p.319-322 (1888)

DUP050066979

DISCUSSION:

Reference 1.

U.S. 1,766,813, H. Eichwede and E. Fischer assigned to General Aniline Works, issued June 24, 1930, claims sulfo aryl pyrazolone carboxylic acid esters and process, comprising condensing an aryl hydrazine sulfonic acid (for example, o-sulfo phenyl hydrazine) with an oxal acetic ester (such as the sodium salt of oxal acetic ethyl ester) and converting the hydrazone thus obtained into the pyrazolone by heating with an alkaline earth carbonate (calcium carbonate).

Reference 2.

U.S. 1,794,218, Wagner, Eichwede & Fischer to General Aniline Works issued February 24, 1931, claims process and products of coupling any diazo compound (specifically o-sulfo amines) with pyrazolones of the type - 1-(4'chlor-5'methyl-2'sulfo phenyl)-5-pyrazolone-3-carboxylic acid or the ethyl ester.

Reference 3.

U.S. 1,819,547, H. Eichwede and E. Fischer assigned to General Aniline Works, Inc., August 18, 1931, covers the azo dyestuffs from sulfo aryl-5-pyrazolone-3-carboxylic acid ethyl ester claimed in Reference 1.

Reference 4.

U.S. 1,874,474, H. Eichwede and J. Rachor, to General Aniline, issued August 30, 1932, covers the yellow azo dyestuffs from pyrazolone derivatives which include 1-phenyl-3-methyl-5-pyrazolone, 1-phenyl-5-pyrazolone-3-carboxylic acid or its ethyl ester coupled to a specific type of amine - as for example meta-amino-benzene sulfonic acid methyl phenylamide.

Reference 5.

U.S. 2,012,553, E. Thoma to General Aniline Works, issued August 27, 1935, claims a process for dyeing by developing with a pyrazolone coupling component which may be a 3-carboxylic acid and its ester or the amide or aryl amide.

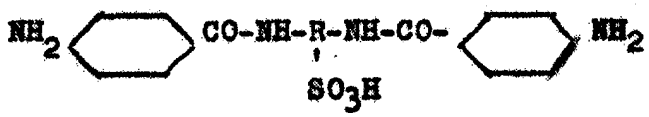
DUP050066980

Reference 6.

U.S. 2,023,953, E. Fischer and H. Kracker to General Aniline Works, issued December 10, 1935, claims mono azo dyestuffs capable of being chromed. A specific claim is for the product of 3-chloro-2-amino benzene-1-carboxylic acid coupled to 1-(2'chloro-5'sulfo phenyl) 5-pyrazolone-3-carboxy ethyl ester.

Reference 7.

U.S. 2,028,439, Clingstein, Roos and Heusner, assigned to General Aniline Works, issued January 21, 1936, discloses 1-(6' sulfo 2'naphthyl)-5-pyrazolone-3-carboxy ethyl ester as a coupling component for disazo dyestuffs, the tetrazo component being of the following formula in which R = Naphthalene radical



Reference 8.

U.S. 2,137,498, H. Mirocourt and M.J.Jiron, assigned to Kuhlman, issued November 22, 1938, claims disazo dyes in which one coupling component is a naphthol sulfonic acid and the other a 1-(sulfo phenyl) 5-pyrazolone which may be 3-methyl, 3-carboxylic acid or an alkyl ester of the latter.

Reference 9.

U.S. 2,228,303, E. Fischer to General Aniline Works, January 14, 1941 claims mono azo dyestuffs of 1-amino-4-ethoxy benzene-5-sulfonyl diethyl amine and 1-phenyl-5-pyrazolone-3-carboxylic acid ethyl ester.Are soluble in organic solvents.

Reference 10

B. 405,003, S. Coffey and R.W. Everett, to Imperial Chemical Industries, issued January 29, 1934, claims process and intermediates as represented by 1-(2':4':6' trihalogen phenyl) 3-methyl (or 3-carbalkoxy)-5-pyrazolones obtained by condensing a trichloro or tribromo phenyl hydrazine with acetoacetic or oxal acetic ester.

DUP050066981

Reference 11

B. 584,255, J.R. Geigy, January 10, 1947, claims red mono azo wool colors obtained by coupling a diazotized 2-aminophenol containing a cyclo alkyl or a 3 to 8C atom alkyl group in the 4 position with a pyrazolone derivative as for example 2-amino-4-tertiary butyl phenol-6-sulfonic acid to 1-(3'chlorphenyl) -5-pyrazolone-3-carboxylic acid ethyl ester. Also discloses the butyl amide of latter.

Reference 12.

D. 629,813 Hans Roos assigned to I.G. Farben, issued May 13, 1936, discloses the azo dyestuff obtained by coupling a mol of tetrazotized amino aryl m- or p-arylene diamine with 1 mol of an aromatic or hydroxy carboxylic acid and with 1 mol of 1-aryl-5-pyrazolone-3- carboxylic acid or derivatives such as esters, amide or aryl amides.

Reference 13.

Belg. 434,679, I.G. Farben, 1940, discloses the coupling of an ether salt of 1-aryl-5-pyrazolone-3-carboxylic acid with a diazotized arylamine devoid of solubilizing groups. The abstract does not further describe the diazo component.

Reference 14.

Wislicenus, Annalen 246,319-322 (1888). A paper on "The Synthesis of Keto Acid Esters. Reference is made to the preparation of 1-phenyl-5-pyrazolone-3-carboxy ethyl ester from phenyl hydrazine and oxal acetic acid. Ring closure is accomplished by warming and no mention is made of the use of any alkali.

Of the above references only Nos. 1 and 10 relate to processes for pyrazolone carboxylic acid esters or the products themselves and in both instances claims are for the sulfo- and the trihalogen phenyl derivatives respectively.

DUP050066982