FIELD OF DISCLOSURE

The present disclosure relates to dioxazine pigments.
More particularly the present disclosure relates to carbazole-dioxazine pigments.

BACKROUND

Carbazole-Dioxazine pigments are well known for its strong bluish-red to violet shade. These pigments have excellent heat, light resistance and outstanding tinctorial strength and used in all applications such as paint, plastic, inks and coatings etc. Pigment Violet 23, is the most important member in this class. Pigment violet-23 (carbazole violet) exhibits color range between bluish-red to violet shade.

However, there is felt a need for developing variants of carbazole–dioxazine pigment so as to exploit the inherent colour strength of dioxazine chromophore with improvement in the pigmentory properties like viscosity, transparency, gloss, heat stability , color strength and durability properties relative to Pigment Violet 23.

OBJECT

It is the main object of the present disclosure to develop a new variant of carbazole–dioxazine pigment having improved pigmentory properties relative to Pigment Violet 23.

Other objects and advantages of the present disclosure will be more apparent from the following description which is not intended to limit the scope of the present disclosure.

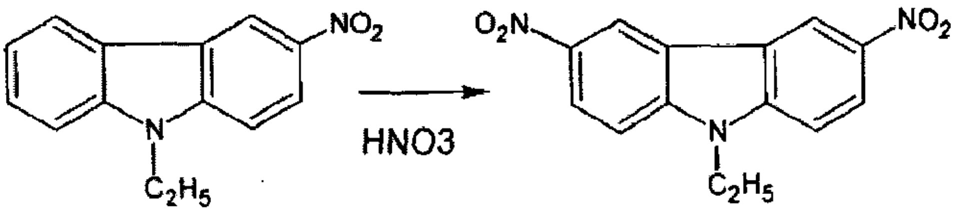
BRIEF DESCRIPTION

The present disclosure provides a high molecular weight carbazole– dioxazine pigment.

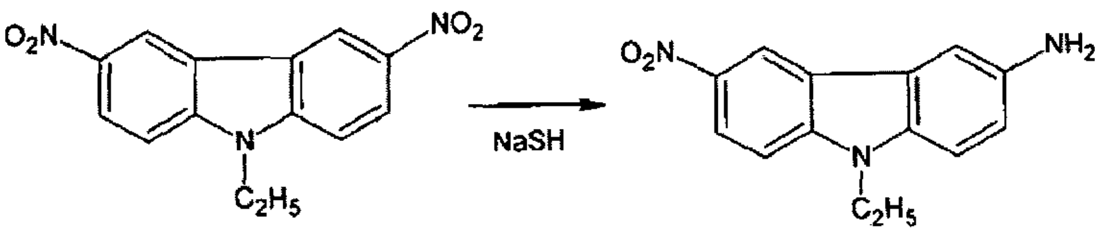
In accordance with the present disclosure there is provided a process for preparing high molecular weight carbazole–dioxazine pigment PV-23 homologue. The PV-23 homologue is prepared from nitro ethylcarbazole (NEC). Nitro ethylcarbazole is nitrated and then partially reduced to yield a mixture containing 3-amino-6-nitro-9N ethylcarbazole which is then further benzoylated with benzoyl chloride to yield 6-benzoylamino-3-amino -9N ethylcarbazole. The benzoyl carbazole on subsequent condensation with chloranil and cyclisation yields high molecular weight carbazole-dioxazine pigment having molecular weight 831, herein referred as PV-23 homologue-II. The molecular weight of PV-23 is 589.

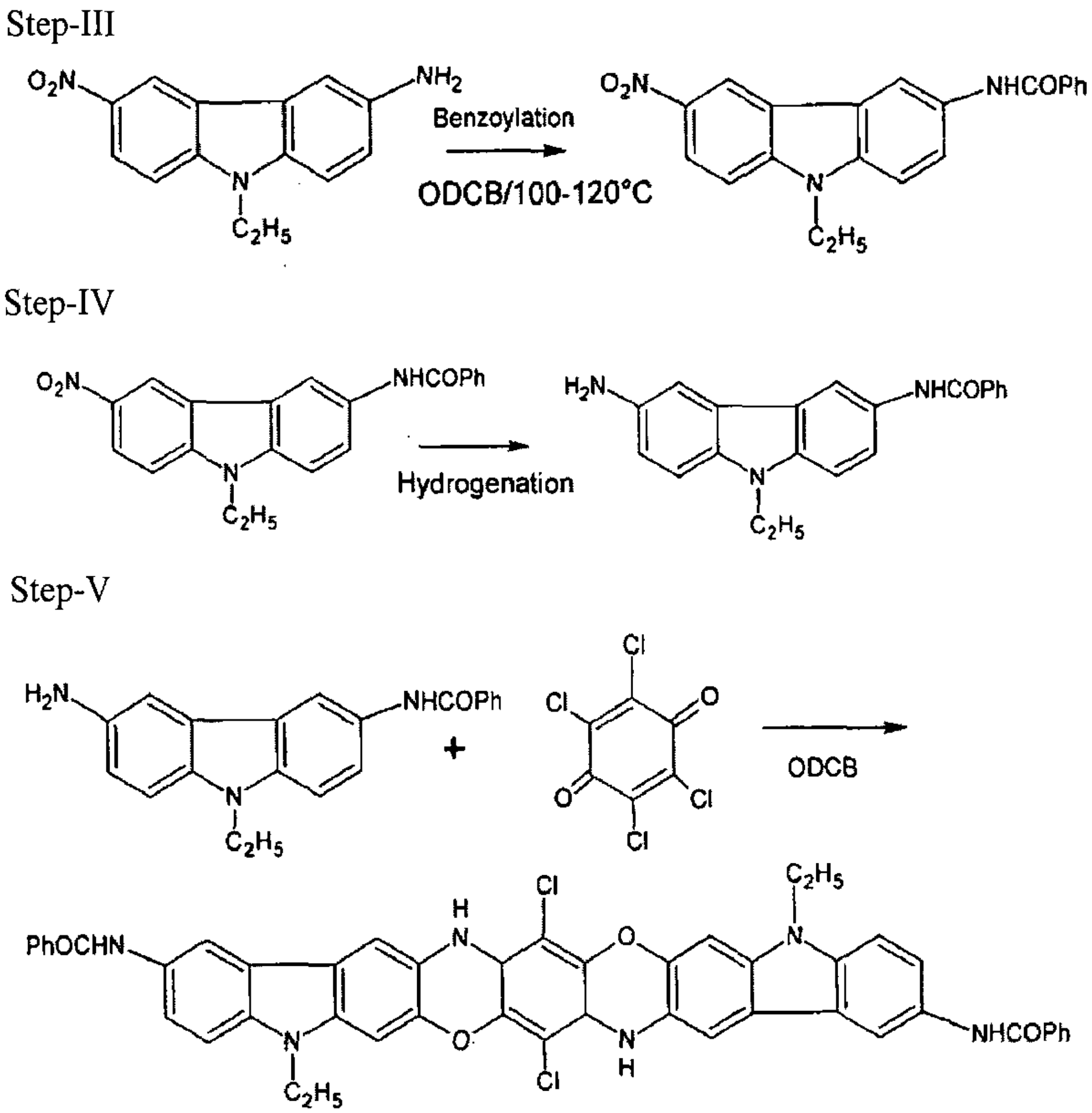
Preparation of high molecular weight carbazole-dioxazine pigment-831 (PV-23 homologue-II) is illustrated with the following schematic diagram:

Step-I



Step-II





Molecular Formula = $C_{48}H_{36}Cl_2N_6O_4$
Formula Weight = 831.74324

Scheme-1

The structure of the synthesized carbazole-dioxazine pigment was confirmed by elemental analysis, IR and NMR spectra. The synthesized pigment was characterized by FTIR spectra. GC-MS and elemental analysis was found to be in agreement with the molecular formula and molecular weight respectively. The physical properties of the pigment were studied. The chemical resistant property was good (in 2% hydrochloric & 2% sodium hydroxide) and solvent fastness (water, xylene, methyethylketone, N-Butanol, PEG, DOP, butyl acetate and mineral turpentine etc.) was found to be excellent. The visible absorption spectrum of the pigment in dimethylformamide was found at λmax 571nm. The study of colour values of the pigment draw-downs were carried out. The CIE attributes of lightness (L*), chroma(C*), hue (h*) and colour (a*, b*) were determined by colorimetric assessment of pigment drawdown.

The disclosure is further illustrated with the help of following working example which should not be construed to limit the disclosure in any way.

Example 1: Preparation of PV-23 homologue-II (831).

Step I: Preparation of 3,6-Dinitro Ethyl Carbazole (DNEC)

Chemicals	Mol Wt	Purity	Qty	Moles	Mole Ratio
Mono Chloro Benzene (MCB)			4800 ml		800 ml
NEC	240	98.5	1440 g	6.0	1.0
$NaNO_2$			4.8 g		0.8 g
Nitric acid	63	68.6	826	9.0	1.5

Nitroethylcarbazole (NEC) 1440gms (6.0moles) was charged in to a reactor vessel containing monochlorobenzene (4800ml) and sodium nitrite 4.8gms. The mixture was then stirred at a temperature 25 to 35^0C. 24 ml nitric acid (9.0moles) was added to the mixture and the mixture was then heated to a temperature range of 75 to 85^0C. 800ml of nitric acid was further added to the mixture over a period of 6-9 hours maintaining the temperature of 75 to 85^0C. Reaction was continued at a temperature of 75 to 85^0C over a period 15-20 hours. The reacted mixture was then cooled, filtered, washed with methyl chlorobenzene followed by water and dried to yield 1245 gms of crude Dinitroethyl carbazole (DNEC 93.1% and NEC-2.1%). Crude DNEC was purified by first dissolving it in nitrobenzene (@ 1gm/ml of nitrobenzene) at a temperature of 160 to 165^0C followed by cooling and filtering to obtain a cake and further reslurring the cake in methanol (@0.95ml/gm of cake) at ambient temperature to obtain pure DNEC of purity 98.6%. The yield of dried product (DNEC) was 1109 gms (64.8%).

Step -II Preparation of Aminonitroethylcarbazole

Chemical name	M.wt	Purity	Wt. Taken gm	Moles	Molar ratio
DNEC	285	98.66	100	0.350	1.0
NaSH solution	56	50%	130ml = 30g	0.535	1.5
Ethanol			200ml		

Sodium hydrosulfide (NaSH) - ethanol solution was prepared by vacuum drying 200 gm of 30% NaSH to remove water and treating it with 200 ml ethanol. To 150 ml of NaSH-ethanol solution so obtained, 100 gm of pure DNEC was charged and the mixture was heated to 65-75^{0}C, further quantity of 110 ml of NaSH ethanol solution was added slowly to the mixture. Reaction was maintained at 65-75^{0}C for 6-7 hours to yield 50% of Aminonitroethylcarbazole (purity 98.3%, DNEC 0.2% and DAEC 0.3%). Elemental analysis of the product so obtained was as follows:

Elemental	%C	%H	%N	%O
Theoretical	65.8	5.09	16.4	12.6
observed	65.8	4.7	16.4	13.2

Step-III: Benzoylation of Aminonitroethylcarbazole

Chemical name	M.wt	Purity	Wt. Taken gm	Moles	Molar ratio
ANEC	255	95	43.2(100%)	0.169	1.0
PhCOCl	140.5	>99	29	0.203	1.2m/m
ODCB			350ml		

A mixture containing 43 gms of Aminonitroethylcarbazole and 350 ml orthodichlorbenzene was heated to 100^{o}C. 29 gms of benzoyl chloride was added to the mixture over a period of 1 hour and the reaction was continued at

100^{0}C. During the reaction evolution of hydrochloric gas was observed. The reaction was carried out for 9-10 hours to yield 87% benzoylated derivative (3-nitro-6-benzoylamino ethyl carbazole) having purity 98.2%. Elemental analysis of the product so obtained was as follows:

Elemental	%C	%H	%N	%O
Theoretical	70.1	5.2	11.69	13.4
observed	69.4	4.4	11.3	14.7

Step IV: Hydrogenation

Chemicals	**M. Wt.**	**% Purity**	**Wt. Taken**	**moles**	**Mole ratio**
Bz-ANEC	359	98.7	50g	0.139	1m
DMAc		99	600ml		
Raney nickel			20g wet cake		
Promoter			*10g*		

50 gms of 3-nitro-6-benzoylamino ethyl carbazole was hydrogenated in the presence of 600ml of DMAc (Dimethyl Acetamide) and 20gm (wet) Raney Nickel at a temperature of 125-130^{0}C and 10-15 kg/cm^{2} for a period of 10-11 hours to yield 82% of the crude hydrogenated product (purity 85-89%). Crude product was recrystallized from DMAc to yield hydrogenated product 3-amino-6-benzoylamino ethyl carbazole of 95% purity. Molecular weight and structure was confirmed by MS, NMR and IR spectra.

Elemental analysis of the product so obtained was as follows:

Elemental	%C	%H	%N
Theoretical	76.59	6.38	12.67
observed	76.65	5.46	11.96

Step V: Condensation and cyclization of 3-amino-6-benzoylamino ethyl carbazole:

Chemicals	M. Wt.	% Purity	Wt. Taken	moles	Mole ratio
3-amino-6-benzoylaminoethylcarbazole	329	95.6	50	0.145	1.0
ODCB			765ml		70gpl
Sodium acetate	136		24.3	0.179	1.23
chloranil	246		26.8	0.109	0.75
BSC	176.5		17.2	0.097	0.67

50gms of 3-amino-6-benzoylamino ethyl carbazole (0.145 moles) and ortho-dichlorobenzene (765 ml) were charged in a reactor vessel. To the mixture sodium acetate 24.3gms (0.179moles) and 26.8 gm chloranil (0.109 moles) was added at a temperature 40 to 45^{0}C, the mixture was then stirred for a period of 10 minutes and heated further to 60-65^{0}C and maintained for a period of 4-6 hours. Reaction was monitored by TLC. After the completion of reaction, acetic acid formed was removed along with ortho-dichlorobenzene by distillation at 60-130^{0}C and 600-670mmHg vacuum, over a period of 3-5 hours. After complete removal of acetic acid, fresh ortho-dichlorobenzene was added followed by addition of 17.2 gms of benzene sulfonyl chloride (0.097 moles). The addition was carried out drop-wise at 140^{0}C over a period of 20 min-1hrs. Temperature was slowly raised to 170 to 175^{0}C and maintained for a period of 6-7 hours to yield a cyclized product. The product mixture so formed was cooled to 90-100°C and then isolated by filtration. The filtered product was washed with hot ortho-dichlorobenzene, with methanol and finally with water and then dried in oven at 80-90^{0}C to yield 56gm of crude pigment (88% yield). The product was characterized by elemental analysis and IR spectra. IR spectra showed absence of amino group.

Elemental analysis	%C	%H	%N
Theoretical	69.25	4.31	10.01
observed	67.61	3.69	9.92

Step VI: Finishing

The dried crude pigment was kneaded and treated with a solvent system containing isobutyl alcohol-water in the presence of caustic lye at a reflux temperature to yield reddish-violet shade of carbazole –pigment having molecular weight-831 and showing following characteristics:

	Illum*	**L***	**a***	**b***	**C***	**h°**
PV 23 Homologue II # 9B2 + #10	D65	56.43	5.615	-18.18	19.03	287.16

Plastic application properties of PV-23 homologue-II:

Properties	**Result**
1. Chemical Resistance to solvents (1-5 Gray scale)	
1. Water	5
2. T-Butanol	5
3. xylene	5
4. Methylethylketone (MEK)	4
5. Toluene	5
2. Chemical Resistance to Acid and alkali (1-5 Gray scale)	
1. 2% acid	5
2. 2% alkali	5

Thus, the chemical resistant property was good (in 2% hydrochloric & 2% sodium hydroxide) and solvent fastness (water, xylene, methyethylketone, N-Butanol, PEG, DOP, butyl acetate and mineral turpentine etc.) was found to be excellent for the carbazole dioxazine pigment developed in accordance with the present disclosure.

Throughout this specification the word “comprise”, or variations such as “comprises” or “comprising”, will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The use of the expression “at least” or “at least one” suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the invention to achieve one or more of the desired objects or results.

Any discussion of documents, acts, materials, devices, articles or the like that has been included in this specification is solely for the purpose of providing a context for the invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the invention as it existed anywhere before the priority date of this application.

While considerable emphasis has been placed herein on the preferred embodiment, it will be appreciated that many embodiments can be made and that many changes can be made in the preferred embodiments without departing from the principles of the disclosure. These and other changes in the preferred embodiments of the disclosure will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation.

Dated this 11th day of June, 2013

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APPLICANTS’ PATENT ATTORNEY