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<p>(54) Title: INORGANIC BLACK PIGMENTS CONTAINING MOLYBDENUM</p>		
<p>(57) Abstract</p> <p>The invention relates to a method of preparing inorganic black pigments using known mixed oxides (spinel) in which Molybdenum or Molybdenum compounds in percentages by weight ranging between 0.05 and 5 % is/are added to said spinels by a calcination process.</p>		

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INORGANIC BLACK PIGMENTS CONTAINING MOLYBDENUM

Inorganic black pigments are used to satisfy a wide variety of needs.

One specific use of inorganic black pigments is related to the manufacture of various ceramic products such as, for instance china tiles, sanitary products and enamelled crockery.

The well known handbook "Classification and chemical description of complex inorganic color pigments" third edition 1991, P.30-33, published by Dry Color Manufacturers Association, 300 North Washington Street, Suite 102, names the following group of inorganic black pigments:

(Cu)[Cr]₂O₄, (C.I. Pigment Black 28)

(Fe, Co)[Fe]₂O₄ (C.I. Pigment Black 29)

(Fe, Co)[Fe, Cr]₂O₄ (C.I. Pigment Black 27)

(Fe, Mn)[Fe, Mn]₂O₄ (C.I. Pigment Black 26)

(Fe, Ni)[Fe, Cr]₂O₄ (C.I. Pigment Black 30)

These compounds are mixed oxides, which in addition to oxygen have two or more metals. They do not have a specific denomination, but are generally referred to as spinels.

The (Fe, Cr)₂O₃ system can also be added to this list since it is widely used to colour ceramics.

The inorganic black pigments belonging to the above systems can contain other metal oxides acting as colour modifiers.

The choice of modifier depends on the specific pigment system.

For example the DCMA handbook mentioned earlier lists the modifiers by the various pigment systems below:

- For Pigment Black 28: Fe₂O₃, MnO;

- For Pigment Black 29: Al₂O₃, B₂O₃, MnO, NiO, SiO₂;

- For Pigment Black 27: CuO, Al₂O₃, B₂O₃, MnO, NiO, SiO₂,

- For Pigment Black 26: TiO₂, CoO, CuO, Al₂O₃, NiO, SiO₂;

- For Pigment Black 30: Mn₂O₃, MnO, CuO.

The influence of these modifiers on the colouring properties of black pigments is not generally very strong and even if it is strong, it is not specific enough.

This is especially apparent when modifiers are present in low concentrations.

In other words, the addition of the aforementioned modifiers cannot obtain significant variations in the desired direction of parameters *L*, *a* and *b* of the

Hunter diagram.

According to the invention process, it has been seen that by calcinating inorganic black pigments with Molybdenum, or with Molybdenum compounds, preferably oxides (Mo_2O_3), the calcination process causes a drastic change in the **L**, **a** and **b** colour values on the Hunter diagram where, as seen in fig. 1, **L** is the coordinate that measures the colour intensity from white to black, **a** is the coordinate that measures the colour intensity from red to green, **b** is the coordinate that measures the colour intensity from yellow to blue of the pigments.

It was also seen that relatively small additions of molybdenum have a greater influence on the **a** and **b** values than on the **L** value.

The **a** and **b** values generally decrease, but the **a** value decreases much more than the **b** value.

It was also seen that, by increasing the addition of molybdenum, the variations in **a** and **b** are relatively smaller.

The process according to the invention gives the possibility of varying colours that characterise the inorganic black pigments of a given composition in exactly the desired direction to improve the pigments, in the sense that a pigment black is obtained which has basically no influence from the other base colours.

In particular, this invention makes it possible to change the **a** value much more effectively than the **b** value. In this way the problem of the different hues of brown found in the majority of inorganic black pigments is solved. This brown hue is usually characterised by a high positive **a** value ($a > 1.00$). The amount of molybdenum that has to be added depends on the pigment system and on the effect that has to be obtained.

To demonstrate the effect that molybdenum has on black pigments, three pigments were chosen from the following systems:

Pigments based on the $(\text{Fe,Cr})_2\text{O}_3$ system are generally used as colours for clays.

Pigments based on the $(\text{Ni, Mn, Fe})[\text{Fe,Cr,Mn}]_2\text{O}_4$ system are generally used as glazes or enamels.

These pigments do not contain cobalt and are therefore less expensive than pigments containing cobalt, in other words based on the $(\text{Co,Ni, Mn, Fe})[\text{Fe,Cr,Mn}]_2\text{O}_4$ system

Experiment: To prepare the pigments containing molybdenum compounds

described in this invention 100 parts by weight of a lot of normal raw pigment that has to be corrected were taken, and the required quantity X of molybdenum compounds was added, being between 0.05 and 5 parts by weight ($0.05 < X < 5$ by weight).

- 5 The mixing, the calcination, the finishing and the testing on the pigment must be conducted with the normal procedures used to produce pigments to be modified.

To clearly show the effect of adding molybdenum, control samples not containing molybdenum are also prepared under the same conditions. The
10 colours for clays containing molybdenum and the control sample are tested during a normal production of tiles.

The (Ni,Mn,Fe)[Fe,Cr,Mn]₂O₄ based glazes or enamels and the control colours are tested in conventional transparent (T) and opaque (O) enamels.

To determine the *L*, *a*, and *b* values of the samples tested, a Minolta CR-331
15 colorimeter was used.

The results are given below:

Example 1: Pigment based on the (Fe,Cr)₂O₃ system (Group of inorganic black pigments used as colours for clays)

- Composition of the control pigment (**A1**):

20 Fe₂O₃ 38.70%

Cr₂O₃ 61.30%

- Composition of the pigment containing molybdenum oxide Mo₂O₃ (**A2**):

100 parts A1 + 0.5 parts A2 (Mo₂O₃)

- 25 Absolute colour values *L*, *a*, *b* of the two pigments in the glaze of the tile (5% pigment by weight)

	A1	A2
L	41.00	39.36
a	0.49	0.18
b	-0.47	-1.10

- 30 It can be seen that the addition of 0.5% by weight of Mo₂O₃ to the pigment decreases considerably all three values *a*, *b* and *L*, giving a more intense pigment without the undesirable red hue.

Example 2: Pigment based from the (Ni,Mn,Fe)[Fe,Cr,Mn]₂O₄ spinel system (group of cobalt-free pigments used as colours for clays)

- Composition of the control pigment (**B1**):

Fe₂O₃ 33.70%

5 Cr₂O₃ 33.70%

MnO₂ 17.70%

NiO 14.90%

- Composition of the pigment containing molybdenum oxide Mo₂O₃ (**B2**):

100 parts B1 + 2 parts Mo₂O₃

10 - *L, a, b* absolute colour values of the pigments in transparent (T) and opaque (O) enamels (5% pigment by weight).

	B1(T)	B2(T)	B1(O)	B2(O)
L	11.00	10.57	52.61	51.50
a	4.70	0.98	1.80	-0.45
b	5.31	2.82	-0.66	-2.67

15 The high *a* value, 4.70, in the transparent enamel, gives it a brown hue. By adding 2% Mo₂O₃ by weight to the pigment, the *a* value drastically decreases to 0.98 and the brown hue disappears.

Example 3: Pigment based on the (Co,Ni, Fe, Mn,)[Fe,Cr,Mn]₂O₄ spinel system (group of black pigments containing cobalt for enamels)

- Composition of the control pigment (**C1**):

20 CoO 24.10%

Fe₂O₃ 26.75%

Cr₂O₃ 27.85%

NiO 8.85%

MnO₂ 12.45%

25 - Composition of the pigment containing molybdenum (**C2**):

100 parts C1 + 2 parts Mo₂O₃

- *L, a, b* absolute colour values of the pigments in transparent (T) and opaque (O) porous glazes:

	C1(T)	C2(T)	C1(O)	C2(O)
L	4.67	6.84	42.40	50.17
a	1.88	0.98	0.79	-0.14
b	1.24	0.14	-4.51	-5.45

Even in this case, by adding 2% by weight of Mo_2O_3 to the pigment, the **a** and **b** colour values are smaller and the pigment becomes a neutral black.

CLAIMS

- 1) Preparation method for inorganic black pigments using known mixed oxides (spinels), **characterised in that** Molybdenum or Molybdenum compounds in percentages by weight ranging between 0.05 and 5% is/are added to said spinels by a calcination process.
- 2) Method of preparation for inorganic black pigments according to claim 1) **characterised in that** the Molybdenum is added under the form of Molybdenum oxide (Mo_2O_3).
- 3) Method of preparation for inorganic black pigments according to claim 2) **characterised in that** the 0.5% by weight of Molybdenum oxide is added.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/04945

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09C3/06 C09C1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 309 173 A (HEINRICH DIEHL) 26 January 1943 (1943-01-26) the whole document ---	1
A	GB 487 078 A (DEUTSCHE GOLD-UND SILBER SCHEIDEANSTALT) 15 June 1938 (1938-06-15) the whole document ---	1
A	US 5 250 112 A (WUSSOW KLAUS ET AL) 5 October 1993 (1993-10-05) the whole document -----	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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