

**Aspects of solid-state chemistry of fly ash
and ultramarine pigments**

by

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ABSTRACT

Ultramarine pigments are aluminosilicate-based and contain sulphur-based chromophores. Several samples from two batches of fine fly ash, a predominantly aluminosilicate waste product of coal combustion, were used successfully to synthesise ultramarine blue. This was confirmed by infrared, Raman and X-ray diffraction results. Fly ash had the advantage of being amorphous, whereas the traditional starting reagent, kaolin, needed to be heat-treated before the ultramarine synthesis to weaken its structure. A comparison of the scanning electron micrographs of fly ash, fly ash treated at 1 000 °C, fly ash reacted with sodium carbonate at 860 °C and the ultramarine products showed that sulphur had a structure-directing effect.

The sulphur clusters found in ultramarine pigments were studied by Self-Consistent-Field Hartree-Fock theory extended by Møller-Plesset second order perturbation theory at the minimum energy with the 6-311G** basis set to determine the relative stability of S_2 , S_2^- , S_2^{2-} , and S_3 , S_3^- , S_3^{2-} . The singly charged species were the most stable in both sets, supporting the hypothesis that the exothermic transition from green to blue ultramarine was the transformation of the doubly charged species to the singly charged species. The open, C_{2v} , isomer was most stable for the S_3^- molecule - the blue ultramarine chromophore. The S_4 molecule was a likely chromophore in ultramarine red. A Woodward-Hoffmann analysis supported the concerted formation of the puckered square S_4 , pyramidal S_4 , and gauche S_4 chain isomers. Other possible species for the red chromophore were S_4^- , S_3 , S_3Cl , S_3Cl^- , S_2Cl , S_2O , and S_2O^- . On the basis of their calculated vibrational spectra most of the species could be discounted as possible red chromophores. The best candidate chromophore was the *cis* S_4 chain based on the computed electronic spectrum.

SAMEVATTING

Ultramarine pigmente is aluminosilikaat gebaseer en bevat swael-gebaseerde chromofore. Verskeie monsters, geneem uit twee lotte fyn stofas, 'n hoofsaaklik aluminosilikaat afvalproduk van steenkoolverbranding, is suksesvol gebruik om ultramarine blou te sintetiseer. Die resultaat is deur infrarooi, Raman en X-straal diffraksie resultate bevestig. Die tradisionele uitgangstof, kaolin, moet eers hittebehandeling ondergaan voordat die kaolin in die sintese van ultramarine gebruik kan word. Stofas is egter reeds amorf en het dus nie vooraf hittebehandeling nodig nie. 'n Vergelyking tussen die mikrofoto van stofas, stofas behandel teen 1 000 °C, stofas gereageer met natrium karbonaat teen 860 °C en die ultramarine produkte het getoon dat swael 'n struktuurrigtende effek het.

Self-Konsistente-Veld Hartree-Fock teorie en Møller-Plesset tweede orde steuringsteorie met die 6-311G** basisstel is gebruik om die relatiewe stabiliteite van S_2 , S_2^- , S_2^{2-} , en S_3 , S_3^- , S_3^{2-} , wat in ultramarine pigmente voorkom, te bepaal. Die enkelgelaaide spesies was die stabielste in beide stelle, ter ondersteuning van die hipotese dat die eksotermiese oorgang vanaf die groen tot die blou ultramarine spesies die omskakeling vanaf die dubbelgelaaide spesie na die enkelgelaaide spesie is. Die oop, C_{2v} , isomeer, is die stabielste S_3^- molekule - die blou chromofoor in ultramarine. Die geslote, D_{3h} , geometrie word as 'n oorgangsfase beskou. 'n Woodward-Hoffmann-ontleding het die meervoudige vorming van die gebuigde vierkantige S_4 , piramidale S_4 , en gauche S_4 ketting isomere ondersteun. Ander moontlike rooi chromofore was S_4^- , S_3 , S_3Cl , S_3Cl^- , S_2Cl , S_2O , en S_2O^- . Op grond van hul berekende vibrasie spektra kan meeste van die spesies as moontlike rooi chromofore uitgeskakel word. Op grond van die berekende elektroniese spektrum was die *cis* S_4 ketting die beste kandidaat.

Psalm 37:3-5:

Trust in the LORD and do good;
dwell in the land and enjoy safe
pasture.

Delight yourself in the LORD
and he will give you the desires of
your heart.

Commit your way to the LORD;
trust in him and he will do this.¹

¹ *The Youthwalk Devotional Bible*, New International Version, Zondervan Publishing House, Grand Rapids, Michigan, p. 568, 1992.

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NOMENCLATURE AS USED BY THE AUTHOR

Compute	Perform a calculation to obtain information on a molecular system.
Calculate	Mathematically determine a descriptive value.
Calcine	Heat a substance to an elevated temperature to facilitate a reaction, for example decomposition reaction.
Sinter	Heat a chemical species in order to facilitate crystallisation or particle growth.
Filler	Substance used to make up volume in a polymeric product.
Pigment	Non-soluble substance that imparts colour to its matrix.
Chromophore	Chemical species responsible for colour.
Ceramic	Inorganic non-metallic compounds that can withstand high temperatures.
Band	Theoretically predicted or experimentally observed absorption in a spectrum.
Peak	Mathematically assigned band, which is described by its position, intensity, width and shape.
ν	Stretch
δ	Deformation
as (subscript)	Antisymmetric
s (subscript)	Symmetric
(IR)	Infrared active
(R)	Raman active
(IR/R)	Infrared and Raman active
(0)	Infrared and Raman inactive
Fa	Fly ash
Fa1000	Fly ash reacted at 1 000 °C
Fa860	Fly ash reacted at 860 °C
FaNa	Fly ash reacted with sodium carbonate

Aluminosilicate	A chemical species in which silica and alumina tetrahedra are linked together to form species similar to those found in silicates. Aluminium silicate is sometimes substituted for aluminosilicate but is not used by the current author.
Crystalline	Used to indicate that a chemical species has long-range structure.
Amorphous	Used to indicate that a chemical species does not have long-range structure. This does, however, not preclude the existence of short-range structure.
Ring size	The ring size in aluminosilicates is the number of tetrahedra that make up the ring, not the number of atoms in the ring.
Microscopic structure	The shape of a particle as observed with a microscope, using either an optical or an electron microscope.
Structure	The sub microscopic structure, that is the relative positions of atoms within chemical species.

PREFACE

To most young researchers the thought of embarking on a research project with the aim of getting a PhD is daunting. This is, however, all too often based on unreliable data as to what is expected of a PhD graduate. Phillips and Pugh² feel that a PhD graduate should become a fully professional researcher, described as follows (quoted from ref 2):

- First, at the most basic level it means that you have something to say that your peers want to listen to.
- Second, in order to do this you must have a command of what is happening in your subject so that you can evaluate the worth of what others are doing.
- Third, you must have the astuteness to discover where you can make a useful contribution.
- Fourth, you must have mastery of appropriate techniques that are currently being used, and also be aware of their limitations.
- Fifth, you must be able to communicate your results effectively in the professional arena.
- Sixth, all this must be carried out in an international context; your professional peer group is worldwide. (It always was, of course, but the rate of diffusion is infinitely faster than it used to be.) You must be aware of what is being discovered, argued about, written and published by your academic community across the world.²

The acceptance of this thesis signifies that the above-mentioned criteria were met.

Several style and format references^{3,4} are available to aid the young researcher. Literature review articles are of great help in starting to map one's path through a research topic. Patent literature is available and opens new avenues of thought. Computer searches of the available literature often yield overwhelming amounts of hits, possibly all important. Searching *The Chemical Abstracts* hard copies seems tedious, but is worth the effort.

2 E.M. Phillips, D.S. Pugh, *How to get a PhD*, Second edition, Open University Press, Buckingham, 1994.

3 Style Manual Committee, Council of Biology Editors, *Scientific Style and Format, The CBE Manual for Authors, Editors, and Publishers*, Sixth edition, Cambridge University Press, Cambridge, 1994.

4 M. O'Connor, *Writing successfully in Science*, First edition, HarperCollinsAcademic, London, 1991.

PUBLICATIONS AND CONFERENCE PROCEEDINGS

A. PUBLISHED ARTICLES

1. Landman AA, De Waal D, **Orbital Symmetry in Sulphur Pigments**, *Crystal Engineering*, 4, pp 159-169, 2001.
2. Landman AA, De Waal D, **Fly Ash as a Potential Starting Reagent for the Synthesis of Ultramarine Blue**, *Materials Research Bulletin*, 39, pp 655-667, 2004.

B. RE-SUBMITTED ARTICLES

Landman AA, De Waal D, **Modelling Sulphur Clusters for an Understanding of Ultramarine**, *South African Journal of Chemistry*.

C. SUBMITTED ARTICLE

Landman AA, De Waal D, **The Nature of the Chromophore in Ultramarine Red: An *Ab Initio* study**, *Journal of Computational Materials*.

D. ARTICLES PREPARED FOR SUBMISSION

1. Landman AA, De Waal D, **A quick reference to fly ash as a valuable resource with many applications, and many more to be developed**, *South African Journal of Chemistry*.
2. Landman AA, De Waal D, **A Scanning Electron Microscope Study of Changes in the Microscopic Structure during the formation of Ultramarine Blue, and the Role Sulphur Plays**, *Materials Research Bulletin*.

E. NATIONAL CONFERENCE CONTRIBUTIONS

E.1. INVITED PAPERS

1. Landman AA, De Waal D, **Skepping van pigmente met Vliegass**, *Akademie vir Wetenskap en Kuns Jong Chemikus*, Bloemfontein, 21 September 1999.
2. Landman AA, De Waal D, **Infrared investigation into the reactions of aluminosilicates**, *Young Spectroscopists Symposium of the South African Spectroscopic Society*, Johannesburg, 26 September 2001.
3. Landman AA, De Waal D, **Modelling ultramarine sulphur chromophores**, 4 July 2002, *SACI2002, 36th Convention of the South African Chemical Institute*, Port Elizabeth, 1-5 July 2002, p s30

E.2. POSTERS

1. Landman AA, De Waal D, **Interpreting Infrared Spectra of Silicates**, *proc SACI2000*, Potchefstroom, 26 September 2000, p 138.
2. Landman AA, De Waal D, **Using The Microscope To Elucidate Sub Microscopic Changes During The Formation Of Ultramarine Pigments**, Johannesburg, December 2001, *proc Microscopic Society of Southern Africa*, 31, p 37, 2001.
3. Landman AA, Boeyens JCA, De Waal D, **The Nature of the Ultramarine Red Chromophore**, *7th Annual Materials Modelling Meeting*, University of the North, Polokwane, 2003.
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F. INTERNATIONAL CONFERENCE CONTRIBUTIONS

F.1. POSTERS

1. Landman AA, De Waal D, **Symmetry in Pigmentary Chromophores**, *Proc INDABA III*, Skukuza, 8 August 2000.

2. Landman AA, De Waal D, **Vanadium electrons in Pigmentary Chromophores**, *Proc INDABA III*, Skukuza, 9 August 2000.
3. De Waal D, Landman AA, Kruger RA, van Schalkwyk J, **Using Raman Spectroscopy to verify pigment identity**, *Proc Seventeenth International Conference on Raman Spectroscopy (ICORS 2000)*, Beijing, China, August 2000.
4. Landman AA, De Waal D, **Vibrational Spectroscopy of Vanadia in Silicates**, *Proc Colloquium Spectroscopicum Internationale (CSI) XXXII*, Pretoria, p P8-9, 10 July 2001.
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