Understanding the Nature and Characteristics of Dark-Black Stains on Rooftops in Uyo Metropolis-Nigeria 1

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Understanding the Nature and Characteristics of Dark-Black Stains on Rooftops in Uyo Metropolis-Nigeria

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ABSTRACT. Understanding the Nature and Characteristics of Dark-Black Stains on Roof-Tops in Uyo Metropolis-Nigeria; a study aimed at knowing the nature and characteristics of dark black stains on rooftops in Uyo metropolis has been undertaken. The study which covered key areas of the town, involved taking samples from rooftops, these samples were sent out for tests using Energy Dispersive X-Ray Fluorescence (ED-XRF), Optical Emission Spectrometer (OES), X -Ray Diffractometer (XRD) and Scanning Electron Microscope (SEM). The tests were carried out on the dark black stains which were scrapped from the rooftops. Tests were also carried out on the sheets, which were directly cut from the roofs. The work was able to establish that the dark black stains on the roofs can be cleaned using soft brush and water. The results of the work equally provided the nature and characteristics of the dark black stains on the surface of roofs in Uyo metropolis. The major components of the dark black stains are alumina (16%), silica (43.80%), carbonaceous and volatile organic matter (16.59%), iron oxide (heamatite) (10.55%), potassium oxide (3.20%), titanium oxide (2.93%) and sulphite (SO_3) (2.71%). The SEM micrographs gave the structure of the dark black stains which were scrapped from the roofs, the structure revealed small shinny white particles, amorphous molecular structure similar to that of polymers and a crystal structure which resembles that formed by carbon and silica. The SEM micrographs also show how the stains are formed on aluminium and zinc substrate. The nature and characteristics of the dark black stains have indicated that using water from these rooftops for direct consumption purpose may have some health implications, and relevant government agencies are requested to investigate the health implications.

Introduction. In an address presented by the governor of Akwa Ibom State, Mr Udom Emmanuel Gabriel at the environment summit organized by the state government at Le Meridien Hotel and Golf Resort, Uyo. The governor lamented the adverse effects of environmental pollution caused by oil flaring and fossil fuels combustion on humans and the environment, he specifically mentioned darkening rooftops in Uyo metropolis which has taken away the aesthetics of many buildings in the state. According to the governor, the problem is so serious that many people are now using dark and black coloured roofing sheets to conceal the black deposits on their roof-tops. The nature of this black deposit is not understood, it is only assumed that it is from gas flaring and combustion of fossil fuels from generators and automobiles. Olajire [13] and Nkwocha [11] also in their respective studies have linked the dark black stains on the roofs to pollution from gas flaring and other industrial activities. Fig. 1-5 clearly captures the menace.

Fig. 1. Building in Uyo Metropolis: The Roof is Completely Covered with Dark-Black Deposit.

Fig. 2. Building Roof Completely Covered with Dark-Black Coating/Deposit.

Fig. 3. Building Roof Completely Covered with Dark-Black Deposit.

Fig. 4. The Roof Top of the Building in the Front is covered with Dark-Black Deposit, the Storey Buildings Behind are Roofed with Dark-colour Roofing Sheets to Conceal the Effect of the Dark-Black Deposit.

Fig. 5. Dark-Black Deposit on Colour Roofs in a Housing Estate in Uyo Town.

Environment means the surroundings in which we live. It is a life-sustaining system in which various living beings like animals, including man, birds, insects, micro-organisms like algae, fungi, protozoa, amoeba and non-living beings like air, water, and soil are inter-related. From time immemorial, the biosphere is discharging faithfully its duty of recycling waste products to make good the loss so that every generation finds it the same as the one before it. According to [2] this self-cleaning and equilibrium maintenance of the biosphere is disastrously disturbed, if waste products released into it exceed its capacity to purify herself. Of late, this is what is happening. We load it with enormous amounts of waste product that the biosphere is becoming more and more poisonous and soon a day will be reached when it becomes inhabitable. When air is polluted, it carries the pollutant with it along the way some of the pollutants are deposited on things with which it comes into contact with. Living things also inhales the polluted air. When it rains the rain washes the pollutants unto roof-tops and down to the soil this explains the interrelationship mentioned above by [2]. Tice [15], Okedere and Elehinafe in their respective works have addressed the effect of air pollution from various sources and associated side effects on structures and living things.

Primitive man ate uncooked food available from plants, birds or animals within his reach. He ate the raw meat. He drank the water from the rivers. He lived in caves or huts made of mud, wood and leaves of some trees. This sort of living never polluted the environment. When Promethenes stole fire, man’s travails began. He used it not only to cook food but also as a weapon to destroy the neighbour-hood. With fire, smoke issuing out was polluting the atmosphere; there was stink. It was in the beginning of the first century that the Roman philosopher Sceneca complained about air pollution. This went on increasing until in the 20^{th} century the Ganges became a death bed for all aquatic animals and the series of air pollution disasters affected millions all over the world [2].

Buildings in Uyo metropolis shortly on completion, the roof gets covered up with dark-black deposits. For reflective roofing sheets they cease to be reflective as a result of this deposits. Jordan Woods [18] of the Berkeley Laboratory notes that reflective roofs are needed for cool buildings [18]. Aesthetics is very important in building structures; aesthetics is now being taken away in most structures shortly after completion by this menace, which requires thorough investigation in order to be able to tackle it. The menace may even have health implication in which case the findings may be of value to the Federal Ministry of Health. In a recent publication by Ihom [5] and [6] the authors observed that WHO has released a report which said that air pollution has become worse in many cities around the world in recent years, especially in Africa and South-East Asia. The UN agency’s report showed that nearly 90 per cent of the world population breathes air that is markedly above the limits recommended by the WHO. Experts from the agency identified car traffic, the burning of coal, oil and gas as well as badly insulated houses as the main culprits. The UN agency had said in April, 2012 that polluted air killed 3.7 million people under the age of 60 in 2012 [17]. Similarly in a publication by Ola [12] the authors observed after their work, which was aimed at indexing pollution in Jos Metropolis that the levels of H_2S, Carbon monoxide and particulate matter were above specified limits for quality air and therefore had some health implications on humans. Understanding the nature of this deposit, which obviously is from the air is therefore very important.

The preceding forms the objective of this work, which is to understand the nature of the dark-black deposits on the surface of roof-tops in Uyo metropolis. The project is part of an Institutional Based Research Work sponsored by Tertiary Education Trust Fund (TETFUND) and it is ongoing.

Materials and method

Materials and Equipment. The materials used for this work included; samples of the dark-black deposits scrapped from roof-tops, samples of test specimens taken from zinc-plated roofing sheet covered with the deposit, samples of test specimens taken from aluminium roofing sheet, and water. The equipment used included; sample cutting scissors, test specimen plastic containers, roof climbing ladder, scrapping tools, Energy Dispersive X-Ray Fluorescence (ED-XRF), Scanning Electron Microscope (SEM), Shimadzu X-ray Diffractometer (XRD) and Optical Emission Spectrometer (OES). Others included, bucket, soft brush and imaging device.

The Study Area. The study area of this research work is Uyo metropolis. Uyo is the Capital of Akwa Ibom state. It is a major oil producing state in Nigeria, with a lot of gas flaring activities going on from the oil exploiting companies. The population of Uyo according to the 2006 Nigerian census which comprises Uyo and Itu is 436,606. The metropolitan area covers an estimated area of 168 km^2 (65sq.mi). Uyo is a fast-growing city and has witnessed some infrastructural growth in recent years. It is located on coordinates $5^0$2`N and $7^0$56’E.

The average annual rainfall in the study area is between 2000-4000mm with the period of fall usually between April and October. The rainfall reaches its peak in the months of June and September, while the dry period falls between November to March. The relative humidity of the area varies between 75% and 95% with mean annual temperatures of about 26 to 36^{o}C. Fig. 6 is the map of the study area. The samples for the work were taken in different areas of the metropolis covering, Use Offot on Nwanniba road, University of Uyo, main campus on Nwanniba road, Ikot-Okubo on Abak road and Mbaibong on Oron road. The town is characterized by high usage of generators as a result of incessant power failure from the national grid and high vehicular traffic typical of a growing metropolis.

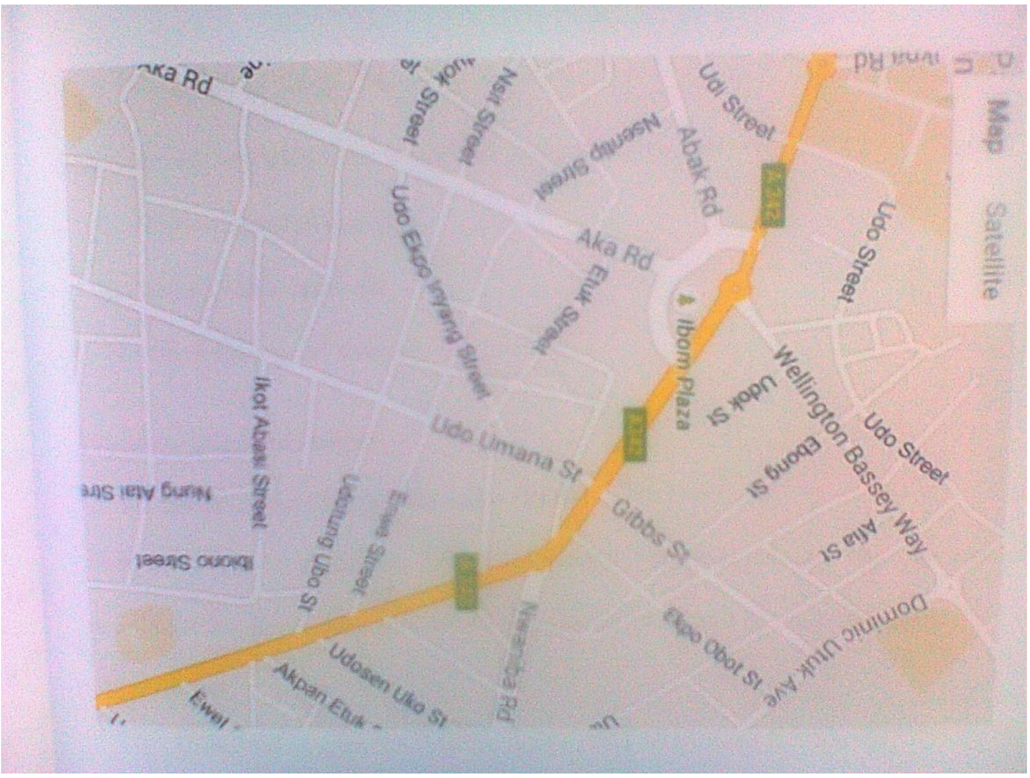


Fig. 6. The Map of Uyo Metropolis the Study Area.

Method. Sample test specimens were taken from roof –tops of buildings in different parts of Uyo metropolis as indicated in the study area above. The samples which were taken included the dark-black coating on top of roofs, which was scrapped from the roof and labeled No1, dark-black coating on zinc coated roofing sheet, labeled No2, and dark-black coating on aluminium base roofing sheet, labeled No3. The last two were cut directly from the roof, see Fig. 9-10. These specimens were sent to National Steel Raw Materials Exploration Agency, Kaduna, Defence Industries Corporation of Nigeria (DICON), and National Metallurgical Development Centre, Jos for analysis. To determine the nature of the dark-black deposit on roof-tops in Uyo-metropolis. Compositional tests were carried out using Shimadzu X-ray Diffractometer (XRD) made in Japan, mini Pal4 ED-XRF (Energy Dispersive X-ray Fluorescence) and Optical Emission Spectrometer (OES). The microstructure of the deposits on the surface of the roof-tops was carried out using Scanning Electron Microscope (SEM).

Critical examinations of the roofs were also carried out using visual examination to ascertain the nature of the deposit and also to establish whether it was living things growing on the roof. Remedial steps were taken to remove the dark-black coating from the roof by cleaning with water and soft brush (See fig. 7-8. No chemical was used for the cleaning, since there was no chemical reaction between the deposits and the roof base. The dark-black deposit was stuck to the roof purely by adsorption, which upon cleaning revealed a clean-shining surface of the roof. See fig.7. Only few growths were seen on the roofs and where they existed the zinc coating was eroded and accompanied by corrosion. The colour of the growth was also different from that of the dark-black deposit.

Fig. 7. Field Work and Sample taking in Progress.

Fig. 8. Roofs showing Reflective Surfaces where test specimens were scrapped from the roofs.

Fig. 9. Transferring Test Samples to Plastic Containers.

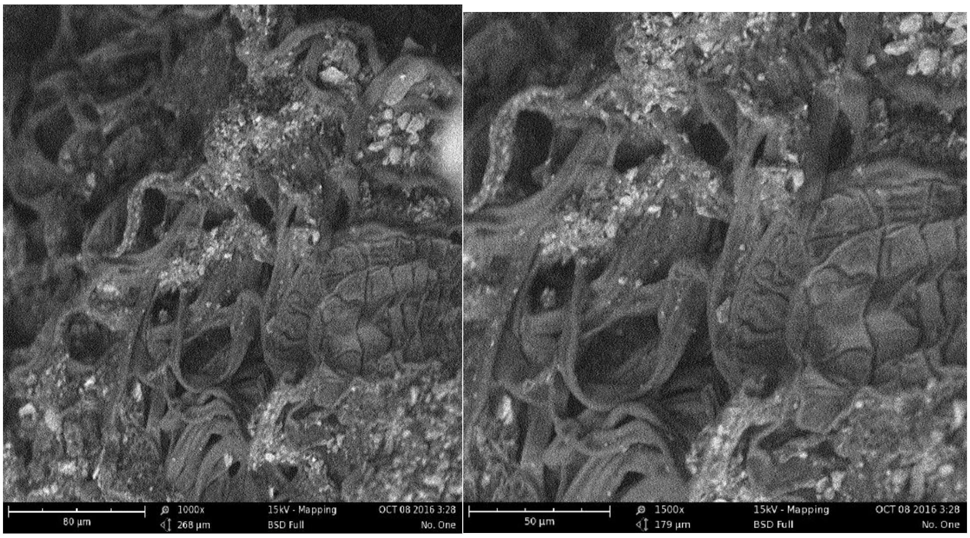
a) b)

Fig. 10. Dark-Black Material Scrapped in (a), Test Specimens cut from the roofs in (b).

Results and discussion

Results. The result of the work is as presented below:

Scanning Electron Microscope (SEM) Micrographs



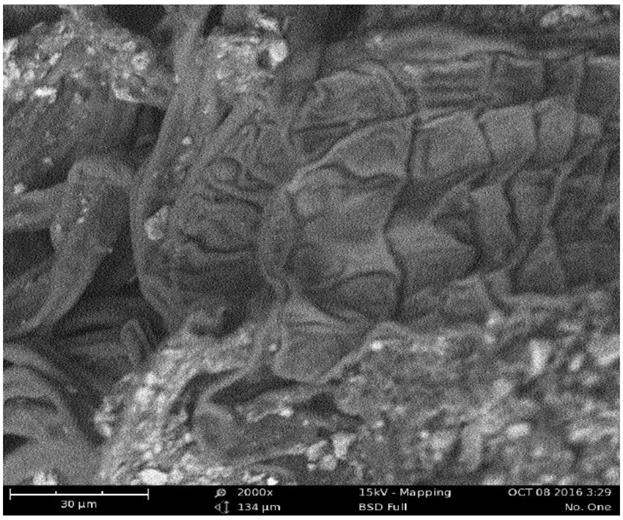


Fig. 11. Scanning Electron Microscope (SEM) Micrographs of the Scrapped Coatings on the Rooftops of Buildings at different magnifications (1000X, 1500X, 2000X).

The micrograph on the Fig. 11 shows that the dark-black material is not a uniform material; small white particles are there, amorphous-like structure like that of the polymer material can be seen and crystal-like structure similar to that seen in some carbon forms can be seen.

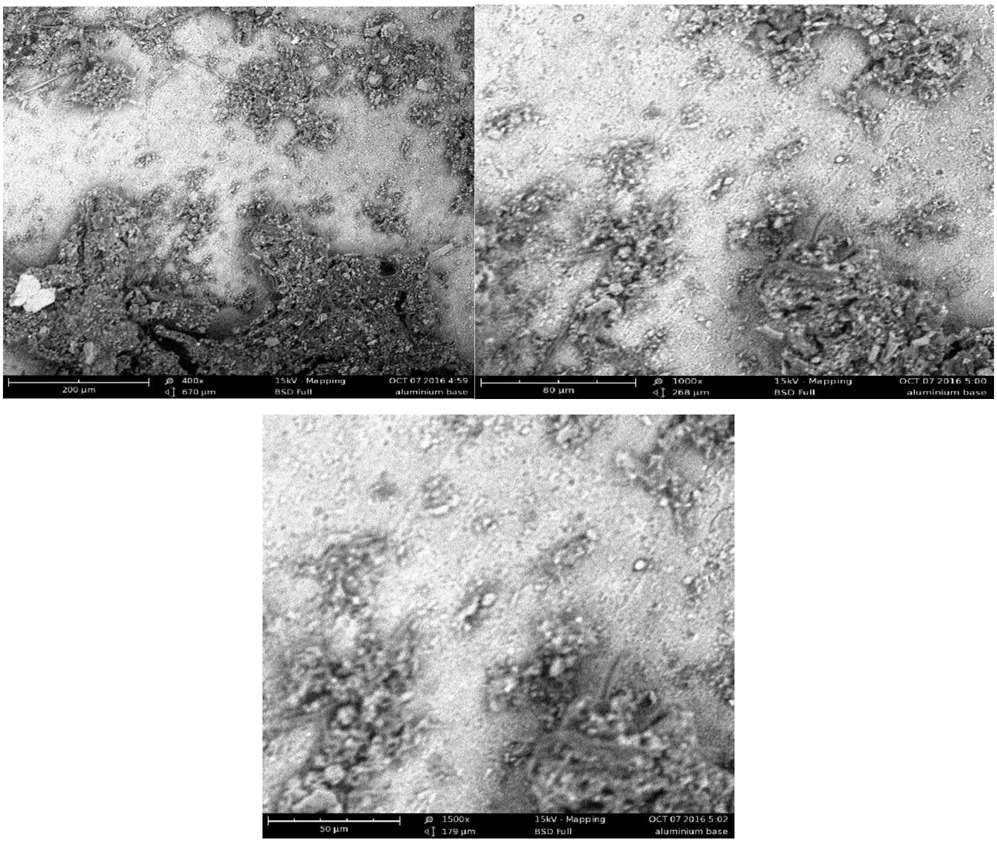


Fig. 12. Scanning Electron Microscope (SEM) Micrographs of dark-black Deposit on Aluminium-base roofing sheet at different Magnifications (400X, 1000X, 1500X). The light shining areas are where the deposit of the material is low and the dark areas are where the deposit has covered the aluminium sheet completely.

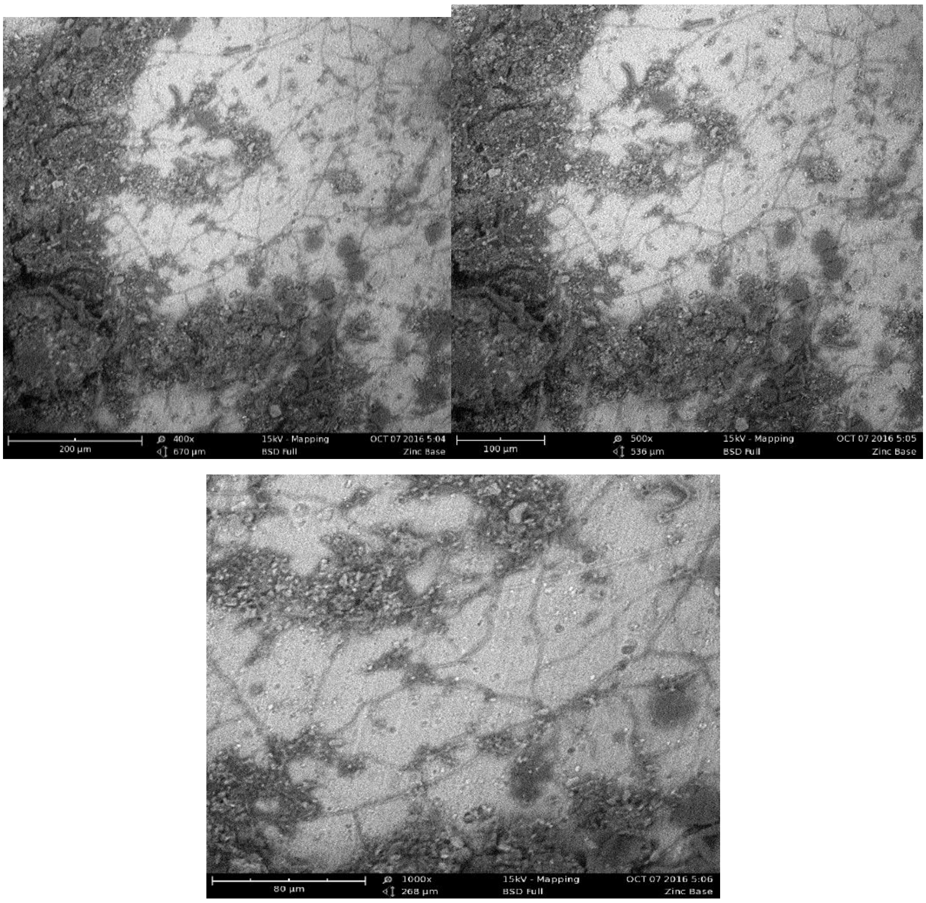


Fig. 13. Scanning Electron Microscope (SEM) Micrographs of dark-black Deposit on Zinc-Coated base roofing sheet at different Magnifications (400X, 500X, 1000X). The light areas have low deposit of the material; the substrate is still shining and the dark areas have large deposit of the material; the substrate is covered.

Chemical Analysis Using ED-XRF

Table 1. Chemical Composition of Dark-Black Material Scrapped from Roof-Tops (Analysed at DICON). Parameters (in %).

S /No	Sample	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	V_2O_5
1	Blackish powder from rooftop	24.10	46.00	1.5	3.16	2.81	1.5	2.48	0.11

Cr_2O_3	MnO	Fe_2O_3	NiO	CuO	ZnO	Yb_2O_3	Re_2O_7	Ag_2O	Eu_2O_3
0.034	0.15	14.49	0.02	0.11	0.15	0.06	0.19	2.87	0.23

Table 2. Chemical Composition of Dark-Black Material Scrapped from Roof-Tops (Analysed at NMDC Jos). Parameters (in %).

S/No	Sample	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	V_2O_5
1	Blackish powder from roof-top	16.00	43.80	1.20	2.71	3.20	1.62	2.93	0.11

Cr_2O_3	MnO	Fe_2O_3	NiO	Co_2O_3	CuO	ZnO	Br	Rb_2O	SrO
0.10	0.31	10.55	0.05	ND	0.09	0.22	0.07	0.03	0.05

ZrO_2	Yb_2O_3	Re_2O_7	PbO	Carbonaceous and volatile matter
0.20	0.001	0.06	0.11	16.59

X-Ray Diffractometer (XRD) Analysis Result on Dark-Black Material Scrapped from Roof-Tops (Analysed at NSRMEA, Kaduna)

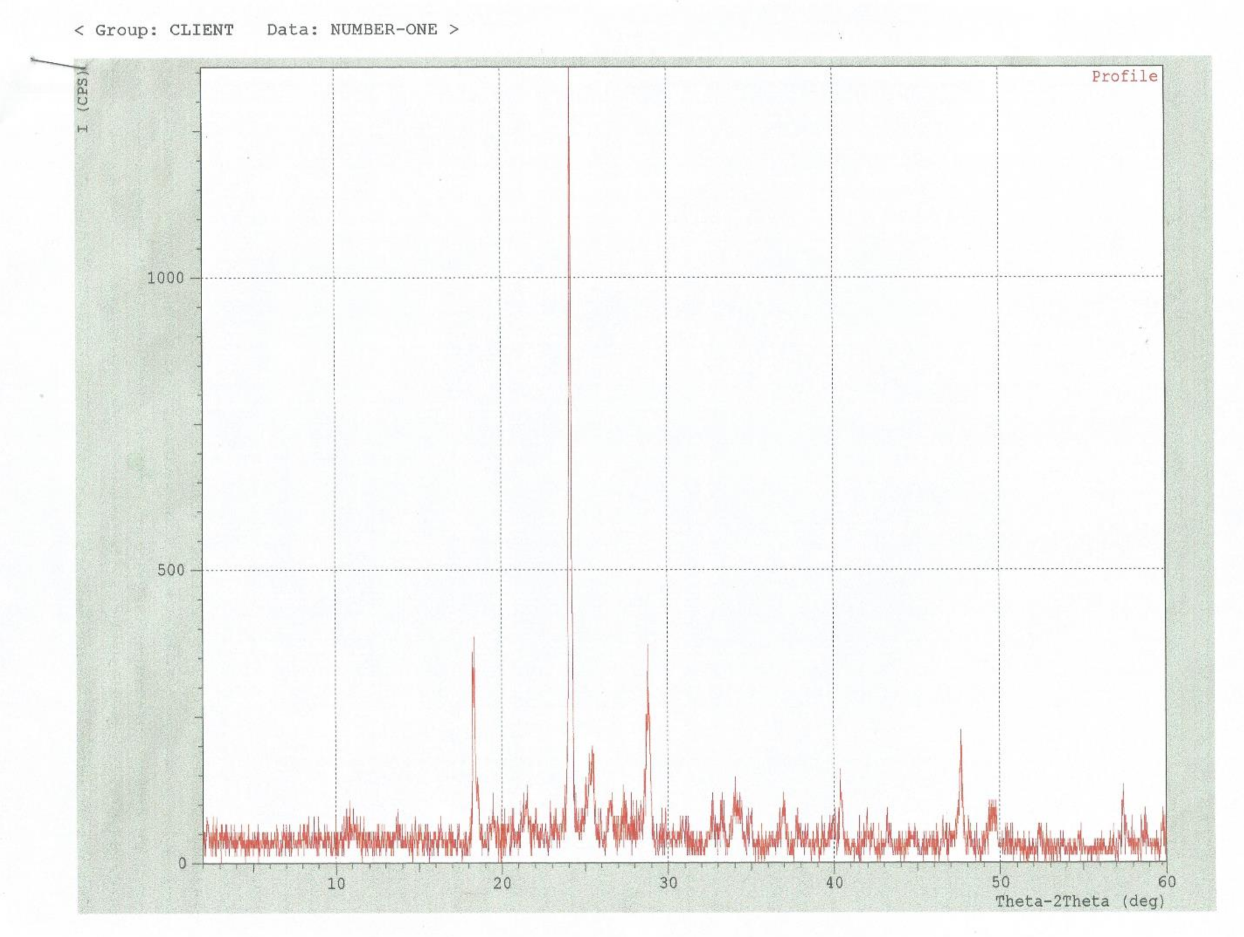


Fig. 14. X-Ray Diffractometer Plot of Intensity against Theta-2Theta for the Dark-Black Material from the Roof-Tops.

********** SEARCH / MATCH RESULT **********

Group Name : CLIENT
Data Name : NUMBER-ONE
File Name : NUMBER-ONE.PSE
Sample Name :
Comment : DARK-BROWN

<Entry Card>

No.	Card	Chemical Formula / Chemical Name (Mineral Name)	S	L / Dx	d / WT%	I / S.G.	R
1	51-1890	K2Ti2O5	0.331	0.643(9/15)	0.730	0.808	0.379
		Potassium Titanium Oxide		-----		-------	
2	21-1272	TiO2	0.114	0.714(5/39)	0.783	0.658	0.368
		Titanium Oxide (Anatase, syn)		-----		-------	
3	47-2217	(C2F4)n	0.259	0.400(4/12)	0.748	0.729	0.218
		Poly(tetrafluoroethylene)		-----		-------	
4	35-0816	CaF2	0.041	0.800(4/16)	0.552	0.437	0.193
		Calcium Fluoride (Fluorite, syn)		-----		-------	
5	39-1352	Zn3(PO4)2.4H2O	0.154	0.571(24/42)	0.686	0.456	0.179
		Zinc Phosphate Hydrate (Parahopeite)		-----		-------	
6	21-1276	TiO2	0.060	0.429(3/38)	0.659	0.597	0.169
		Titanium Oxide (Rutile, syn)		-----		-------	
7	26-1079	C	0.111	0.600(3/16)	0.745	0.360	0.161
		Carbon (Graphite-3\ITR\RG, syn [N)		-----		-------	
8	16-0613	Mgx(Mg,Fe)3(Si,Al)4O10(OH)2.4H2O	0.194	0.517(15/32)	0.650	0.416	0.140
		Magnesium Iron Aluminum Silicate Hydroxide		-----		-------	
9	10-0492	KMg3(Si3Al)O10(OH)2	0.204	0.833(20/26)	0.700	0.228	0.133
		Potassium Magnesium Aluminum Silicate Hydr		-----		-------	

*** Basic Data Process ***

Group : CLIENT
Data : NUMBER-ONE

Strongest 3 peaks

no.	peak no.	2Theta (deg)	d (A)	I/I1	FWHM (deg)	Intensity (Counts)	Integrated Int (Counts)
1	16	24.1893	3.67637	100	0.15350	134	1224
2	6	18.3839	4.82214	22	0.19720	30	291
3	28	28.8474	3.09245	19	0.25500	26	340

Peak Data List

peak no.	2Theta (deg)	d (A)	I/I1	FWHM (deg)	Intensity (Counts)	Integrated Int (Counts)
1	2.6792	32.94936	4	0.09330	5	30
2	10.7424	8.22901	4	0.07670	5	28
3	14.8404	5.96460	3	0.09000	4	32
4	16.3963	5.40194	3	0.11000	4	48
5	17.4641	5.07398	3	0.07000	4	22
6	18.3839	4.82214	22	0.19720	30	291
7	18.6272	4.75970	7	0.12000	9	70
8	19.5143	4.54528	4	0.10000	6	60
9	20.7208	4.28327	3	0.12000	4	43
10	21.2344	4.18081	4	0.05000	5	16
11	21.3989	4.14904	3	0.12000	4	22
12	21.5386	4.12245	5	0.10000	7	43
13	22.1022	4.01858	4	0.07000	5	29
14	22.9585	3.87060	3	0.07330	4	20
15	23.2546	3.82198	3	0.08000	4	19
16	24.1893	3.67637	100	0.15350	134	1224
17	25.1108	3.54351	5	0.08000	7	35
18	25.2905	3.51873	8	0.09000	11	61
19	25.4901	3.49163	9	0.14660	12	106
20	26.0225	3.42139	3	0.06670	4	14
21	26.3287	3.38229	3	0.08000	4	15
22	26.5284	3.35728	5	0.20000	7	68
23	26.6781	3.33878	5	0.10000	7	54
24	27.3071	3.26329	4	0.08000	5	36
25	27.4719	3.24408	4	0.05000	5	23
26	28.4255	3.13738	3	0.08000	4	24
27	28.6252	3.11595	8	0.10000	11	50
28	28.8474	3.09245	19	0.25500	26	340
29	29.9034	2.98560	3	0.08000	4	25
30	30.9472	2.88724	3	0.09000	4	22
31	31.1020	2.87322	3	0.04000	4	12
32	32.6203	2.74287	3	0.06000	4	43
33	32.7401	2.73311	3	0.00000	4	0
34	33.2621	2.69140	5	0.08500	7	46
35	33.8340	2.64721	3	0.09000	4	20
36	34.0188	2.63325	6	0.12000	8	42
37	34.1787	2.62129	4	0.16000	5	39
38	34.3585	2.60799	4	0.12000	6	40
39	35.0179	2.56037	4	0.10000	6	35
40	36.9961	2.42788	4	0.20000	6	75
41	37.7705	2.37986	3	0.05000	4	22
42	39.3243	2.28934	3	0.10000	4	26
43	39.9689	2.25389	4	0.07000	5	23
44	40.4386	2.22879	9	0.13000	12	89
45	41.9975	2.14959	4	0.13000	6	67
46	42.2524	2.13721	3	0.08000	4	36
47	43.2118	2.09195	5	0.08000	7	44
48	47.4894	1.91302	3	0.00000	4	0
49	47.6343	1.90754	13	0.17000	17	161
50	48.1491	1.88834	3	0.08000	4	22

Fig. 15. X-Ray Diffractometer (XRD) Analysis Result on Zinc Coated Roofing sheet Covered with Dark-Black Material (Analysed at NSRMEA, Kaduna).

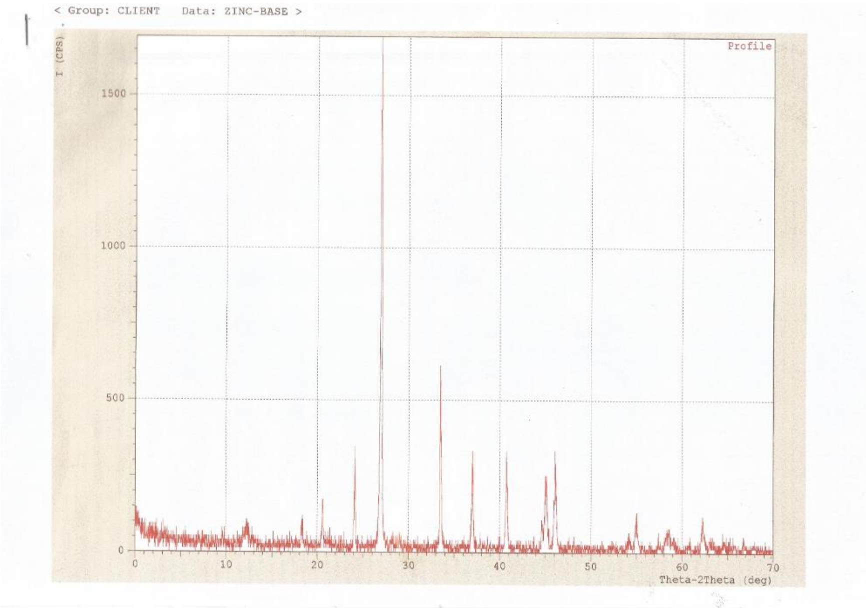


Fig. 16. X-Ray Diffractometer Plot of Intensity against Theta-2Theta for the Zinc Coated Sheet Covered with Dark-Black Material.

```
Group Name  : CLIENT
Data Name   : ZINC-BASE
File Name   : ZINC-BASE.PSE
Sample Name :
Comment     : GREY
<Entry Card>
No.  Card     Chemical Formula                          S      L          d     I    R
              Chemical Name (Mineral Name)                     Dx   WT%   S.G.
 1  34-0369 CrB2                                   0.179 0.600( 3/20) 0.802 ----- 0.481
            Chromium Boride                                 -----          -------
 2  6-0695 Fe3Al                                   0.412 0.500( 3/11) 0.611 ----- 0.305
            Aluminum Iron                                   -----          -------
 3  34-0140 FeCr2O4                                0.265 0.333( 3/27) 0.602 ----- 0.201
            Iron Chromium Oxide ( Chromite, syn )           -----          -------
 4  18-0877 (Fe,Ni)                                0.696 0.353( 6/25) 0.530 ----- 0.187
            Iron Nickel ( Unnamed mineral [NR] )            -----          -------
 5  35-0783 Cr23C6                                 1.000 0.250( 4/28) 0.740 ----- 0.185
            Chromium Carbide                                -----          -------
 6  26-0571 CuZn                                   0.850 0.333( 3/13) 0.550 ----- 0.183
            Copper Zinc                                     -----          -------
 7  9-0459 Zn2Mn4O8.H2O                            0.321 0.278( 5/32) 0.608 ----- 0.169
            Zinc Manganese Oxide Hydrate ( Hydrohetaer      -----          -------
 8  34-0001 Fe3C                                   0.251 0.263( 5/24) 0.632 ----- 0.166
            Iron Carbide ( Cohenite, syn )                  -----          -------
 9  23-1418 Tb2O3                                  0.368 0.375( 9/37) 0.441 ----- 0.165
            Terbium Oxide                                   -----          -------
10  35-0803 Cr2N                                   0.950 0.333( 3/23) 0.483 ----- 0.161
            Chromium Nitride                                -----          -------
11  4-0712 CaC2                                    0.661 0.250( 3/25) 0.637 ----- 0.159
            Calcium Carbide                                 -----          -------
12  10-0446 Al2Si2O5(OH)4                          0.324 0.231( 9/39) 0.685 ----- 0.158
            Aluminum Silicate Hydroxide ( Dickite-2\IT      -----          -------
```

Group : CLIENT
Data : ZINC-BASE

Strongest 3 peaks

no.	peak no.	2Theta (deg)	d (A)	I/I1	FWHM (deg)	Intensity (Counts)	Integrated Int (Counts)
1	4	26.9812	3.30196	100	0.18010	173	1746
2	7	33.5238	2.67099	33	0.13490	57	445
3	3	24.1577	3.68111	17	0.16000	30	262

Peak Data List

peak no.	2Theta (deg)	d (A)	I/I1	FWHM (deg)	Intensity (Counts)	Integrated Int (Counts)
1	18.3825	4.82250	5	0.23000	8	101
2	20.6310	4.30171	9	0.14000	15	133
3	24.1577	3.68111	17	0.16000	30	262
4	26.9812	3.30196	100	0.18010	173	1746
5	27.2538	3.26955	3	0.09330	6	50
6	29.0646	3.06983	3	0.08000	5	29
7	33.5238	2.67099	33	0.13490	57	445
8	37.0077	2.42715	16	0.19670	28	294
9	40.7596	2.21197	17	0.16460	30	294
10	44.6959	2.02588	5	0.13000	9	63
11	45.0923	2.00898	12	0.30330	21	304
12	45.4305	1.99481	3	0.04000	5	21
13	46.0971	1.96751	17	0.20600	29	366
14	54.9861	1.66861	5	0.20000	9	129
15	58.3999	1.57894	3	0.07000	5	49
16	62.2836	1.48949	6	0.16000	11	110

Fig. 17. X-Ray Diffractometer (XRD) Analysis Result on Aluminium Alloy Roofing Sheet Covered with Dark-Black Material (Analysed at NSRMEA, Kaduna).

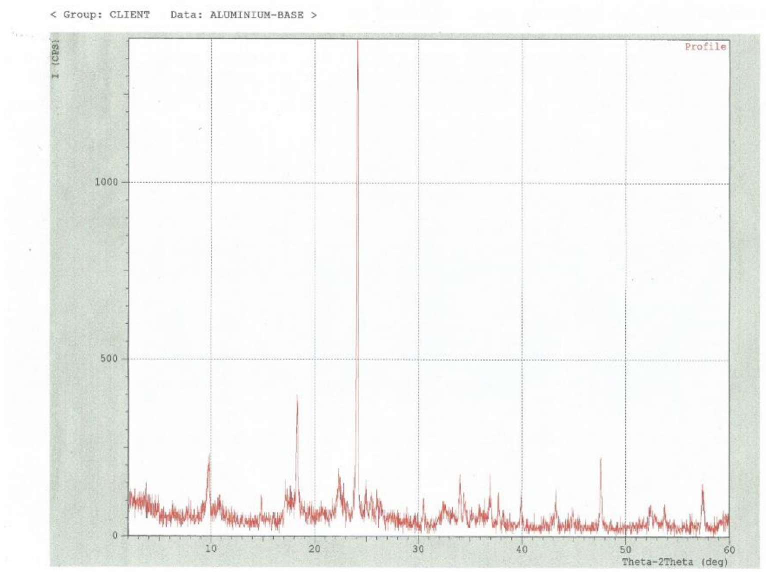


Fig. 18. X-Ray Diffractometer Plot of Intensity against Theta-2Theta for the Aluminium Roofing Sheet Covered with Dark-Black Material.

Group : CLIENT
Data : ALUMINIUM-BASE

Strongest 3 peaks

no.	peak no.	2Theta (deg)	d (A)	I/I1	FWHM (deg)	Intensity (Counts)	Integrated Int (Counts)
1	13	24.1362	3.68434	100	0.15110	227	1943
2	6	18.3653	4.82698	21	0.15540	48	440
3	31	47.6327	1.90760	15	0.12220	35	250

Peak Data List

peak no.	2Theta (deg)	d (A)	I/I1	FWHM (deg)	Intensity (Counts)	Integrated Int (Counts)
1	9.7615	9.05360	7	0.09340	16	112
2	9.9003	8.92698	10	0.18280	22	194
3	14.9284	5.92964	5	0.10670	11	102
4	17.2296	5.14251	4	0.08000	10	64
5	17.3693	5.10146	4	0.13340	10	92
6	18.3653	4.82698	21	0.15540	48	440
7	22.1571	4.00875	4	0.12000	8	67
8	22.3716	3.97080	7	0.23000	17	177
9	22.6359	3.92503	3	0.10000	7	45
10	22.8155	3.89454	4	0.12000	8	64
11	23.1623	3.83700	4	0.06500	9	50
12	23.7735	3.73972	3	0.05000	7	32
13	24.1362	3.68434	100	0.15110	227	1943
14	24.9816	3.56154	5	0.10900	12	77
15	25.4926	3.49130	4	0.08500	9	56
16	26.0691	3.41538	4	0.12000	9	55
17	26.3736	3.37663	3	0.11000	7	91
18	30.5542	2.92348	7	0.11670	15	114
19	30.7590	2.90448	4	0.07330	8	41
20	32.4105	2.76015	4	0.10000	8	88
21	34.0421	2.63150	8	0.16670	19	167
22	34.4292	2.60279	6	0.09170	13	65
23	34.5916	2.59094	4	0.09330	10	50
24	36.9422	2.43130	7	0.18210	16	140
25	37.7870	2.37886	6	0.11300	14	83
26	38.2551	2.35082	4	0.09340	8	44
27	39.9432	2.25528	7	0.11470	17	114
28	40.1903	2.24198	3	0.07330	7	32
29	43.2833	2.08866	7	0.12330	17	155
30	44.9583	2.01466	4	0.11500	8	63
31	47.6327	1.90760	15	0.12220	35	250
32	52.3272	1.74697	4	0.10000	10	68
33	52.4671	1.74264	4	0.10000	8	64
34	53.7649	1.70359	4	0.14330	10	93
35	57.4372	1.60309	11	0.13600	25	201

Group Name : CLIENT
Data Name : ALUMINIUM-BASE
File Name : ALUMINIUM-BASE.PSE
Sample Name :
Comment : GREYISH SAMPLE

<Entry Card>

No.	Card	Chemical Formula / Chemical Name (Mineral Name)	S	L (Dx)	d (WT%)	I (S.G.)	R
1	35-0787	Mo2C Molybdenum Carbide	0.246	0.750(3/13) -----	0.707	0.874 -------	0.463
2	10-0173	Al2O3 Aluminum Oxide (Corundum, syn)	0.094	0.556(5/42) -----	0.797	0.697 -------	0.309
3	10-0325	NiFe2O4 Nickel Iron Oxide (Trevorite, syn)	0.480	0.875(7/23) -----	0.701	0.503 -------	0.309
4	1-1236	Fe3N Iron Nitride	0.166	0.750(3/15) -----	0.824	0.431 -------	0.266
5	34-0140	FeCr2O4 Iron Chromium Oxide (Chromite, syn)	0.392	0.857(6/27) -----	0.576	0.533 -------	0.263
6	36-1249	Fe2C Iron Carbide	0.174	0.750(3/ 5) -----	0.859	0.396 -------	0.255
7	21-1272	TiO2 Titanium Oxide (Anatase, syn)	0.205	0.857(6/39) -----	0.597	0.413 -------	0.211
8	24-1047	NaAl2(AlSi3)O10(OH)2 Sodium Aluminum Silicate Hydroxide (Parag	0.554	0.391(9/25) -----	0.804	0.612 -------	0.192
9	6-0399	BaZrO3 Barium Zirconium Oxide	0.135	0.667(4/17) -----	0.506	0.519 -------	0.175
10	22-0539	Ca3Si2O7 Calcium Silicate (Rankinite)	0.197	0.452(14/31) -----	0.712	0.498 -------	0.160
11	12-0041	NiS Nickel Sulfide (Millerite)	0.164	0.583(7/31) -----	0.597	0.456 -------	0.159

Fig. 19. X-Ray Diffractometer (XRD) Analysis Result.

Table 3. Optical Emission Spectrometer (OES) Analysis Result of the Aluminium Alloy Roofing Sheet Covered with Dark-Black Material (Analysed at DICON, Kaduna). Parameter (in %)

Element	**Cu**	**Si**	**Mg**	**Zn**	**Fe**	**Mn**	**Ni**	**Ti**	**Cr**
%	1.9924	16.182	5.6218	7.5650	0.75939	1.0102	3.0453	0.11968	0.50535
Sn	**Pb**	**V**	**P**	**Al**	**Ba**				
0.16975	0.11760	0.10747	-	59.24	3.46				

Discussion. The method and the results of this work have been well presented and from the method it was established that the attachment of the dark-black material onto roof-tops is more of a physical thing than chemical. The deposits can be scrapped and it can also be cleaned with water and a soft brush without affecting the surface of the roofing sheets. The few growth of living things sighted occurred where the zinc coating on the roofing sheet had cracks. In such areas corrosion was also noticed. Other growths noticed on top of the deposits had no effect on the zinc coated roofing or the aluminium roofing sheets. This observation is in complete agreement with previous studies which had said that the presence of zinc, copper granules and aluminium salts discourages algae, fungal, moss and lichens growth [1], [4], [18]. According to InspectApedia.com [7], dark black or brown roof shingle stains are often caused by black algae, bleed-through or extractive bleeding of asphalt, dirt, soot, or organic debris. However, there are other roof stain colors and causes. Dangelo [4] said: "Just like wearing lighter colored clothing, a lighter colored shingle can reduce roof temperatures by 50 degrees or more". An added benefit is that white or light colored roofs benefit the environment as well. Dark-black stained roofs reduce the reflectiveness of roofs thereby making buildings to be hot requiring the use of air-conditioning systems.

The objective of this work is to understand the nature and characteristics of the dark-black stains on rooftops in Uyo metropolis. Water harvesting from rooftops is a common practice in Nigeria and therefore establishing the nature of this dark-black stains, which mixes with the water, is imperative. On this premise SEM micrographs were taken of the dark-black stains scrapped from the roof tops, dark-black stains on aluminium roofing sheet and dark-black stains on zinc coated roofing sheets (see Fig. 11-13). The micrographs (Fig. 11) which were taken at different magnifications revealed that the dark-black stains were not of uniform composition, but consisted of small white particles, amorphous-like molecular structure like that of the polymer material and a crystal-like structure similar to that seen in some carbon forms [8].

Chemical analysis using ED-XRF was carried out on the dark-black stains scrapped from the rooftops. The samples were sent to two different institutions for comparison so as to establish reliable result (see Tables 1-2). The dark-black stains from visual observation were sooty in nature. The two results have some compounds that are usually found in soot. The dark-black deposit is from the particulates in the air as well as the soot particles in the air. Gas flaring, the use of generators, and vehicular traffic releases emissions in the surrounding under study. The result from DICON Kaduna is higher than that from NMDC Jos in some of the parameters measured this may be because the analysis from DICON Kaduna did not take cognizance of organic, carbonaceous and volatile matter. The result from NMDC Jos however, assigned a total of 16.59% to this components. The result from NMDC Jos is therefore more reliable. In the two results the highest components of the dark-black stain powder scrapped from the roofs are SiO_2, Al_2O_3, Fe_2O3, Carbonaceous and volatile organic matter, K_2O, TiO_2 and SO_3 see Tables 1-2 for detail percentages. Dara [3] said, that owing to particulates large surface areas, particulates provide excellent sites for absorption of various organic and inorganic species which encourage heterogeneous phase reactions in the atmosphere. Particulates include Fe_2O_3, V_2O_3, CaO, $PbCl_2$, $PbBr_2$, fly ash, aerosols, soot etc. polycyclic aromatic hydrocarbons (PAH) are important constituents of several organic particulates which are carcinogenic. Soot is a highly condensed product of PAH compounds and can itself adsorb many PAH compounds and toxic trace metals e.g Be, Cd, V, Ni, and Mn as well as carcinogenic organics such as benzo-α-pyrenes [3]. The last sentence agrees with the analysis results in Tables 1-2.

X-Ray Diffractometer (XRD) Analysis was also carried out on the dark black stains scrapped from the roof, dark-black stains on zinc substrate and dark-black stains on aluminium substrate, which were taken directly from the roofs (see Figs. 14-16). The X-Ray Diffractometer analysis of the scrapped dark black stains showed that in addition to the composition given by ED-XRF; the dark-black stains contained polytetrafluoroethylene, Calcium Fluoride, zinc phosphate hydrate, carbon (graphite) and magnesium. This result explains the structure seen in the SEM micrographs for the dark-black stains; the polytetrafluoroethylene may be responsible for the amorphous polymer structure seen and the carbon may be responsible for the carbon structure sighted in the SEM. The Zinc phosphate hydrate was scrapped along with the dark-black stains when samples were taken. This compound is normally at the surface of zinc coated roofing sheets. The XRD identification of components present in the dark black stains scrapped from roof-tops agreed with composition of soot and particulate as stated by [3].

The only new compounds in the analysis of the dark-black stains on zinc and aluminium substrate are chromium nitride, molybdenum carbide, and barium oxide. The chromium nitride indicate the presence of nitrogen. The molybdenum carbide indicate the presence of molybdenum on the substrate. The barium oxide indicate the presence of barium on the substrate. Table 3 which is the result of chemical analysis of the aluminium alloy roofing sheet using Optical Emission Spectrometer, confirms the presence of barium.

The above discussion have shown that the deposits on rooftops in Uyo metropolis are from particulates and soot. The health implications of these pollutants have been highlighted in the work by Okedere and Elehinafe who worked on the effect of suspended particulate matter from diesel generators. Other authors like Kirby [9], Mendez [10], Person and Kucera [14] have discussed rooftop stains and quality of water from the rooftops in their respective works. Of concern from the present study to health is SO_3, and polytetraflouroethylene which have health implications as shown by Dara [3], the other metals which are present in the dark black stains and also known to be associated with toxicity are actually in small quantities and may only cause problem over an extended period of exposure or usage of water from the roof tops.

Summary. The study titled “Understanding the Nature and Characteristics of Dark-Black Stains on Roof-Tops in Uyo Metropolis-Nigeria” was extensively and elaborately undertaken and considered to truly understand the true nature and characteristics of these dark black stains which have become an eye saw on rooftops in Uyo metropolis. The following findings and conclusions were drawn from the work:

1. The dark black stain/ covering on the rooftops is as a result of polluted atmosphere which is polluted with particulates, aerosols and soot these gets deposited on rooftops

2. The dark black stains are physically adsorbed or adhered to the roof and can be cleaned using water and soft brush.

3. The major components of the dark black stain are alumina, silica, carbonaceous and volatile organic matter, iron oxide (heamatite), potassium oxide, titanium oxide and sulphite (SO_3).

4. The dark black color is from the soot which contains carbon and other organic compounds and normally absorbs other particulates too. This explains the large compounds present in the dark black stain.

5. Finally, the wide range of tests carried out on the dark black stain on the rooftops have established that the components of health concern are SO_3 and the polytetrafluoroethylene. The other metallic components are in small quantities and may have health implication only after extended use of water from these rooftops.

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