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The Potentials of Waste Organic Materials for Surface Hardness Improvement of Mild Steel.

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Abstract

The study has investigated the potential of some organic waste materials for surface hardness improvement of mild steel. Waste organic materials like sugar cane, rice husks, egg shell, melon shell, arecaceae flower droppings, plastics, polyethylene, and charcoal were used during the study. These materials were prepared in various shapes and sizes before mixing them with mild steel specimens and heat treating in the furnace at 920^{o}C. The specimens were heated to 920^{O}C for 5 hours and then quenched in water. They were then tested for hardness using Rockwell hardness testing machine. The result in each case showed great improvement over the control specimen. The highest value of hardness was obtained with arecaceae flower droppings and egg shell combination, which had a value of 56.6 HRC, followed by arecaceae flower droppings only, with 56HRC, melon shell and egg shell followed with 52.6HRC, melon shell alone had 47.8HRC, and results of the other organic materials also showed improvement over the control specimen value of 30HRC. The microstructural examination of the specimens showed a sharp contrast between the treated and untreated specimen. The effective case depth of the specimen from the arecaceae was determined and the value obtained was 0.70mm, that of arecaceae with egg shell was 0.75mm and that of melon shell and egg shell was 0.65 mm. These values of effective case depth were good and can provide protection to the mild steel for a long time. The results have established the potentials of waste organic materials for surface hardness improvement of mild steel. The waste organic materials used in the casehardening media all showed improvement in the hardness values of the mild steel specimens over the 30 HRC hardness value of the untreated mild steel specimen.

Keywords: case hardening, improvement, mild steel, potential, surface hardness, waste organic materials.

1 INTRODUCTION

Is there anything that is really a waste? May be not, and this may explain why environmental experts are emphatically stressing on recycling of waste to reduce the waste burden on planet earth [1]. We are in a period of economic transition. The 'cowboy economy' of the past is obsolescent, if not obsolete. Environmental services are no longer free goods, and this fact is driving major changes [1]. A clean environment contributes to healthy living, this fact has since been realized by developed countries like Japan and many other European countries. These countries have succeeded in integrating clean environment into their cultures [2]. The reverse is the case with most developing economies of the world; in Nigeria for instance a visit to any of the major cities presents obnoxious situation, rubbish, garbage, polythene, plastic wastes, metal scraps, and industrial waste are seen littering the streets. Some of these wastes form breeding places for mosquitoes and other vectors that spread sicknesses. This is a very serious cause for concern and this quotation by Dara [3] makes sense in checkmating this ugly situation; in his words 'in a fragile biosphere, the ultimate fate of humanity may depend on whether we cultivate a deep sense of self-restraint, founded on a widespread ethic of limiting consumption and finding non-material enrichment'. The tremendous increase in industrial activity during the last few decades and the release of obnoxious industrial wastes into the environment, have been of considerable concern in recent years from the point of view of environmental pollution. Solid waste management is very poor in most developing nations, this is because it comprises of purposeful and systematic control of the generation, storage, collection, transport, separation, processing, recycling, recovery, and disposal of solid waste; most developing countries lack both the capacity and the will power to manage solid waste [3].

The research into metal property improvement will continue particularly surface finishing technology for metal property improvement; this is because of man's quest to produce durable machines, with high performance and high quality [4]. Different materials are used in order to enhance the surface finish of metals the type of material used depends on the technique and type of surface finish desired. Surface finishing processes include coatings, impregnation of surfaces of metals with different elements, heat treatment and others [5].

Impregnation of metal surfaces with different elements include proceses like carburization, carbonitriding, and nitriding, which in recent years have undergone a lot of transformation in terms of practice and methods [5].

Waste organic materials contain such elements as carbon, nitrogen, hydrogen, oxygen, sulphur, silicon etc which most times exist in combined form called compounds [6]. When these organic materials are subjected to high temperatures; decomposition occurs releasing nascent element which is picked at the surface of the steel; the high temperature facilitates the diffusion of the element into the steel. Municipal wastes include household solid wastes, among these wastes could be found egg shells and bones these are rich sources of calcium carbonates. The use of calcium carbonate as energizer in casehardening of mild steel has been confirmed by many including these present authors [6],[7].The use of municipal and agricultural solid waste in metallurgy and materials engineering is steadily increasing sugar cane bagasse has been used for aluminum alloy particulate composite as well as for case hardening of mild steel [6],[7],[8].

Because of the high temperature and the presence of oxygen in the furnace atmosphere oxidation takes place on the surface of the steel. Just underneath the oxide layer the elements combined with others to form compounds this gives rise to what is called compound layer this layer sometimes increases with age hardening, after this layer is the diffusion layer which is made up of elements which have diffused into the steel, this results into the straining of the metal structure and it is responsible for the increase of hardness and strength of the steel. The compound and diffusion layers of the treated steel are normally very hard [9].

The objectives of this work are to determine the potential of waste organic materials for surface hardness improvement of mild steel, to examine the microstructural changes on treatment with the organic material, to determine the effective case depth after treatment and finally to take note of the improvement recorded after the use of the organic materials as surface hardeners.

2 MATERIALS AND METHODS

2.1 Materials / Apparatus

The egg shells that were used in the work were collected from waste dump at Asak village of Plateau state. The mild steel was obtained from the producers in Kaduna state of Nigeria. Waste sugar cane, rice husks, waste plastics, waste polyethylene bags, and melon shell were sourced at a waste dump in Jos. Charcoal was source

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from burnt tree in the village of Asak, while ammonia was from NMDC heat treatment laboratory. Groundnut oil was bought at Faringada market in Jos. Arecaceae flower droppings were collected at National Metallurgical Development Centre Jos directly under the plants. Consumables for metallography were those of the NMDC metallographic laboratory. Table 1 shows the chemical composition of the steel used.

TABLE 1

CHEMICAL COMPOSITION OF THE STEEL USED.

Element	C	Si	Mn	P	S	Cr	Ni	Mo	Al	Cu	Co	Ti	Nb
%	0.25	0.19	0.70	0.06	0.03	0.08	0.04	0.01	0.01	0.26	0.01	0.002	<0.01
Element	V	W	Pb	B	Sn	Zn	As	Bi	Ca	Ce	Zr	La	Fe
%	0.002	0.02	0.006	0.001	0.02	0.005	0.006	<0.02	0.006	0.004	0.002	0.004	98.1

2.1.1. Apparatus

The equipment/apparatus used for the research included the following: Rockwell hardness testing machine, electric tubular furnace, hand blower, lathe machine, grinding mill, casehardening boxes, quenching baths, metallographic equipment, and hacksaw.

2.2 Methods

2.2.1 Materials preparation

The melon shells, sugar cane waste, and egg shells were pulverized using a grinding mill. The charcoal was reduced to small size by pounding in a metal mortar with a steel pestle. The plastics and the polyethylene wastes were reduced by cutting into pieces using a knife. The arecaceae flower droppings were however, not pulverized. The mild steel was cut to 20mm x 20mm, it was then washed in acetone and rinsed in water to remove dirts. It was then dried using warm air from hand blower. For each of the carburizing materials; two carburizing boxes were used, one containing only the carburizing material embedded with the mild steel. The second box was filled with the carburizing materials and 50g of egg shell. Except for ground nut oil mixed with rice husks, waste plastics and polyethylene waste bags, and charcoal mixed with ammonia. The lids to the carburizing boxes were then replaced and sealed using clay paste to avoid air ingress so that oxidation will not take place.

2.2.2 Carburizing process

The carburization operation was carried out using an electric tubular furnace. The carburization was carried out at a temperature of 920^{o}C and a holding time of 5 hours. The furnace had automatic control; once the data was entered the operation subsisted only for the entered data. The quenching was done in water immediately after removal from the furnace to avoid temperature drop.

2.2.3 Hardness profile

Hardness profiles of the test specimens were measured using Rockwell hardness testing machine. The scale C was selected for the test measurements. The hardness tests were performed on the samples in accordance with the standard of hardness testing of metallic materials as per DIN 50103; ISO/ R80; JIS Z 2245: 2005 and ASTM E18 based on Rockwell hardness ‘C’ scale [10],[11]. The hardness tester used was Frank hardness tester welltest 38506 designed in accordance with DIN51224, and ISO/ R716. A minor load of 10 kg (98.07 N) was applied first to seat the brale, after which a major load of 150 kg (1471N) was applied for the indentation. Three indentations were made on each test specimen and the average was calculated for the resultant hardness. At the beginning of the test the hardness tester was checked with a standard block of 59.6HRC to ensure that the machine was not out of calibration. These precautions are very important for accurate result. Some of the specimens were selected and hardness profiles were obtained at an interval of 0.5 mm this was used to get the effective case depth of the specimens.

2.2.4 Microstructure examination

One of the carburized specimen and the un-carburized mild steel were cut, ground and polished. A belted grinding machine with grits 240-600 was used. The specimens were then transferred to a pre-polishing disc where alumina powder paste of 1 micron was used for pre-polishing. The specimens were finally polished on the finishing disc; 0.5 micron of alumina paste was used. It was ensured that the surfaces were devoid of scratches and it was thoroughly washed and dried using a hand blower to avoid chemical corrosion. 2% nital solution was used to etch the specimen and rinsing was done using clean water. It was then dried using a blower before transferring to the microscope for viewing and taking of the photomicrograph of the microstructure.

3 RESULTS AND DISCUSSION

3.1. Hardness and case depths

The results of the research are as presented in Tables 2-3, Figure 1 and Plates 1-2. The un-carburized mild steel has a hardness value of 30 HRC.

Table 1, show the chemical composition of the steel which was used for the case hardening process. The carbon content of the steel is 2.5% which makes it a low carbon steel with the required characteristics for casehardening. The steel conforms to JIS B 6914:2002 standards for steels to be carburized [12]. Table 2 shows the carburizing agents and the hardness values produced by the carburizing agents on the mild steel. Nine different compositions are shown in the table and the result has shown that they have produced different hardness values on the treated mild steel specimen. The chemical composition of the carburizing materials is no doubt not the same likewise the elements that dissociated during the case hardening process, rice husk apart from being rich in silicon also has carbon; under high temperature treatment silicon has the tendency to also diffuse into the steel just like carbon in a process called siliconization [13]. The untreated steel has a hardness value of 30 HRC however; specimens treated with the wastes in Table 2 all have values that are greater than 30 HRC a clear indication that the wastes are potential materials for carburization of mild steel. The result of the hardness test showed that the hardness value produced by the mixture of the wastes and egg shell was higher than when the waste was used alone. Sugar cane waste produced a hardness of 45.1HRC but when it was mixed with egg shell the hardness became 45.5. Melon shell waste produced a hardness of 47.8 HRC on the mild steel but when it was mixed with egg shell the hardness became 52.6 HRC. Arecaceae flower waste produced a hardness value of 56 HRC on the mild steel specimen but when it was mixed with egg shell the hardness produced on the mild steel specimen became 56.5 HRC. The result has shown that egg shell waste is an enhancer in the carburization of mild steel. Egg shell contains $CaCO_3$ and the use of carbonates like calcium carbonate, barium carbonate, sodium carbonate as energizers in pack carburization have been explained by many [6, 14-16]. The mechanism of the carburization process is summarized in the equations below:

$$CO_2 + C \longrightarrow 2CO \quad (2)$$

$$CaCO_3 \longrightarrow CaO + CO_2 \quad (3)$$

$CO_2 + C \longrightarrow 2CO$ (Carbondioxide from Eq 3)

$$2CO \longrightarrow C + CO_2 \quad (4)$$

$$CaO + CO_2 \longrightarrow CaCO_3 \quad (5)$$

$$3Fe + 2CO \longleftrightarrow Fe_3C + CO_2 \quad (6)$$

$$Fe_3C + 2H_2 \longleftrightarrow 3Fe + CH_4 \quad (7)$$

$$3Fe + CO + H_2 \longleftrightarrow Fe_3C + H_2O \quad (8)$$

The rate of diffusion of carbon into the steel will depend on the carburizing temperature, the composition of the carburizing mixture, and the type of steel. A case depth of about 0.2mm may be obtained after 1 hour at 900^{O}C, but in practice, the carburizing rate becomes progressively slower. Both temperature and time are important factors in carburizing. The carbon content in the case becomes higher as temperatures are increased. The case depth progresses with time but not in direct proportion to it. The wastes decomposes at the high carburizing temperature releasing a mixture of gases, nitrogen, hydrogen, carbonmonoxide, carbondioxide, and also leaving behind a carbonaceous substance. The calcium carbonate in the egg shell also decomposed as in eq3. The carbondioxide produced by the wastes and the decomposed egg shell combined with the carbon from the wastes to form carbonmonoxide. The carbonmonoxide dissociate on the surface of the steel, producing nascent carbon which diffuses into the steel as in eq 4 and eq 6. Meanwhile the calcium oxide produced during the decomposition of calcium carbonate recombines with carbondioxide to produce calcium carbonate again. This reaction helps in raising the carbon potential of the carburizing mixture as the calcium carbonate decomposes again more carbonmonoxide is produced and nascent carbon is again deposited on the surface of the steel and the carburizing process continues. The hydrogen in the carburizing atmosphere reduces the carbon in the steel, but in the presence of sufficient carbonmonoxide nascent carbon is deposited on the steel surface and the hydrogen is oxidized to steam, see equations 7 and 8. The carbon deposited on the surface of the steel is dissolved by the austenite phase of the steel and diffuses into the steel which on subsequent quenching in water develops a hard case [6],[11],[15]. The reactions taking place with the steel are equilibrium reactions, since they may go either way depending upon the chemical make-up of the carburizing mixture [6],[11]. Ground nut oil and rice husk wastes produced a hardness value of 45.5 HRC, wastes plastics and polyethylene wastes produced a hardness value of 47.0 HRC on the mild steel, and charcoal and ammonia mixture produced a hardness value of 43.8 HRC on the mild steel specimen. The hardness values all showed improvement over the 30HRC value of the untreated mild steel. The overall result of Table 2 is an indication of the potentials of organic waste materials for surface hardness improvement of mild steel. The mechanism responsible for the surface hardness improvement of the mild steel given the wide range of media used is indeed a complex one suffice to say that two things are responsible; one is the carbon potential which according to JIS G 0201 is carbon content at the surface of a specimen of pure iron in equilibrium with the carburizing medium considered [12]. The other is the nature of the case formed both in structure and in chemical composition. The different media have different atmospheres; in the presence of some oxygen, oxides are produced in the compound layer which is defined by JIS G 0201 as surface layer formed during a thermochemical treatment and made up of the chemical compounds formed by the element(s) introduced during the treatment and certain elements from the base metal, this layer may consist of nitrides during nitriding, carbides during carburizing and siliconizing etc [12]. Just underneath the compound layer is the diffusion layer or diffusion zone which is the surface layer formed during a thermochemical treatment containing, in solid solution or where appropriate partially precipitated, the element (s) introduced during the treatment. The content of these elements diminishes continuously as the core is approached. The precipitates in the diffusion zone can be nitrides, carbides, etc (see plate 1) [9]. The last layer is the core of the steel which

Surface Finishing Engineers call the substrate [11].

The depth of case hardening is normally influenced or determined by the carbon potential (activity) of the carburizing medium. The higher the carbon potential, the higher the equilibrium carbon concentration at the surface of the steel, and thus the deeper the carburizing depth [6],[9],[14]. Thus the role of an energizer is thought to be related to its ability to raise the carbon potential of the carburizing medium. This explains why in all the carburizing mixtures with egg shell the result showed improvement in the hardness value over the carburizing mixtures without egg shell. How an energizer does this has not been clearly outlined and indeed why only a particular energizer should be a more effective energizer is still a matter of some conjecture though chemical stability is thought to be an important factor [16].

Table 3 shows the effective case depth produced on the steel specimens by three of the carburizing materials which have high hardness values sufficient to use ASM Committee's specification for measuring effective case depth according to the Committee, 'effective case depth is the perpendicular distance from the surface of a hardened case to the farthest point at which a hardness of 50 HRC is measured' [11]. Arecaceae flower with egg shell produced the highest effective case depth of 0.75 mm on the steel specimen and is followed by arecaceae waste alone with an effective case depth of 0.7 mm. Melon shell wastes with egg shell produced an effective case depth of 0.65mm. This result further strengthens the position of other results that egg shell is an enhancer in the carburization of mild steel. The result of table 3 has further confirmed the potentials of the organic wastes as materials for surface hardness improvement of mild steel with the reasonable effective case depth produced on the surface of the mild steel.

The diffusion of carbon proceeds from the higher concentration at the work-piece surface to the lower concentration at the core [6],[11],[16]. When consistent concentrations (surface and core) are maintained, the depth of case may be predicted for any constant temperature of operation, for this work the total case depth was predicted to be 1.34mm based on the input data provided above.

Figure 1, has clearly illustrated the potentials of waste organic materials for surface hardness improvement of mild steel. The chart shows that arecaceae flower waste with egg shell has the highest hardness value of 56.6HRC followed by arecaceae flower waste alone. Melon shell waste with egg shell then followed, and then melon shell waste, which is then followed by waste plastics and polyethylene wastes, sugar cane waste and egg shell medium, and groundnut oil and rice husk medium, has the same value of 45.5 HRC, sugar cane waste medium then followed, and lastly, came charcoal and ammonia medium with hardness value of 43.8HRC. The carburization mechanism was explained above and the reason for the different hardness values can be linked to the variation in the carbon potential of the carburizing materials and as explained in the introduction [6],[9],[11].

3.2 Microstructure

The hardness of a steel material is related to its macro and microstructures and the composition of the zone or layer of the treated steel specimen measured [17]. For a casehardened steel specimen the composition of the compound layer or what some people wrongly call the white layer is different from the diffusion layer and so the substrate or core of the steel specimen

[12],[17]. This can be seen in plate 1 which was selected from the many samples treated. The area captured in the micrograph is within the compound layer and the diffusion layer, precipitates and martensite can be seen in the structure as explained above. Plate 2 is the microstructure of the untreated mild steel specimen showing pearlite structure in a ferritic matrix a sharp contrast from the structure of plate 1.

4 CONCLUSION

The results have established the potentials of waste organic materials for surface hardness improvement of mild steel. The waste organic materials used in the casehardening media all showed improvement in the hardness values of the mild steel specimens over the 30 HRC hardness value of the untreated mild steel specimen.

TABLE 2

HARDNESS VALUES OF MILD STEEL CARBURIZED WITH WASTE CARBONACEOUS MATERIALS AND WASTE CARBONACEOUS MATERIALS MIXED WITH EGG SHELL.

S/NO.	Wastes/Indentations	1	2	3	Average Hardness value (HRC)
1	Sugar cane waste	45.3	43.8	46.3	45.1
2	Sugar cane +Egg shell	47.8	43.8	44.8	45.5
3	Melon shells waste	49.8	46.8	46.8	47.8
4	Melon shells +Egg shell	53.3	51.8	52.8	52.6
5	Aracaceae flower wastes	56.3	55.3	56.3	56.0
6.	Aracaceae + Egg shell	58.3	55.3	56.3	56.6
7	Groundnut oil + rice husks	45.8	44.8	45.8	45.5
8	Waste plastics + polyethylene	50.8	44.8	45.3	47.0
9	Charcoal + ammonia	45.8	41.8	43.8	43.8

TABLE 3

EFFECTIVE CASE DEPTH OF SOME OF THE CARBURIZING WASTE MATERIALS EXTRACTED AT 50 HRC FROM THE SURFACE OF THE CARBURIZED STEEL SPECIMENS.

Carburizing Material	Hardness (HRC)	Effective Case Depth (mm)
Melon shell + Egg shell	52.6	0.65
Aracaceae flower waste	56.0	0.70
Aracaceae waste + Egg shell	56.6	0.75

Using the carburizing temperature, time and proportionality factor that varies with temperature the theoretical case depth was estimated using the formula

$d = \Phi\sqrt{t}$ (1) [7],[11]

Where, d = total case depth, t = carburizing time in hours = 5hours

Φ = depth factor in mm/ $\sqrt{h}$ = 0.6 at 920^{o}C

Inserting the above data in Eq 1, the theoretical total case depth = $0.6\sqrt{5} = 1.34$ mm

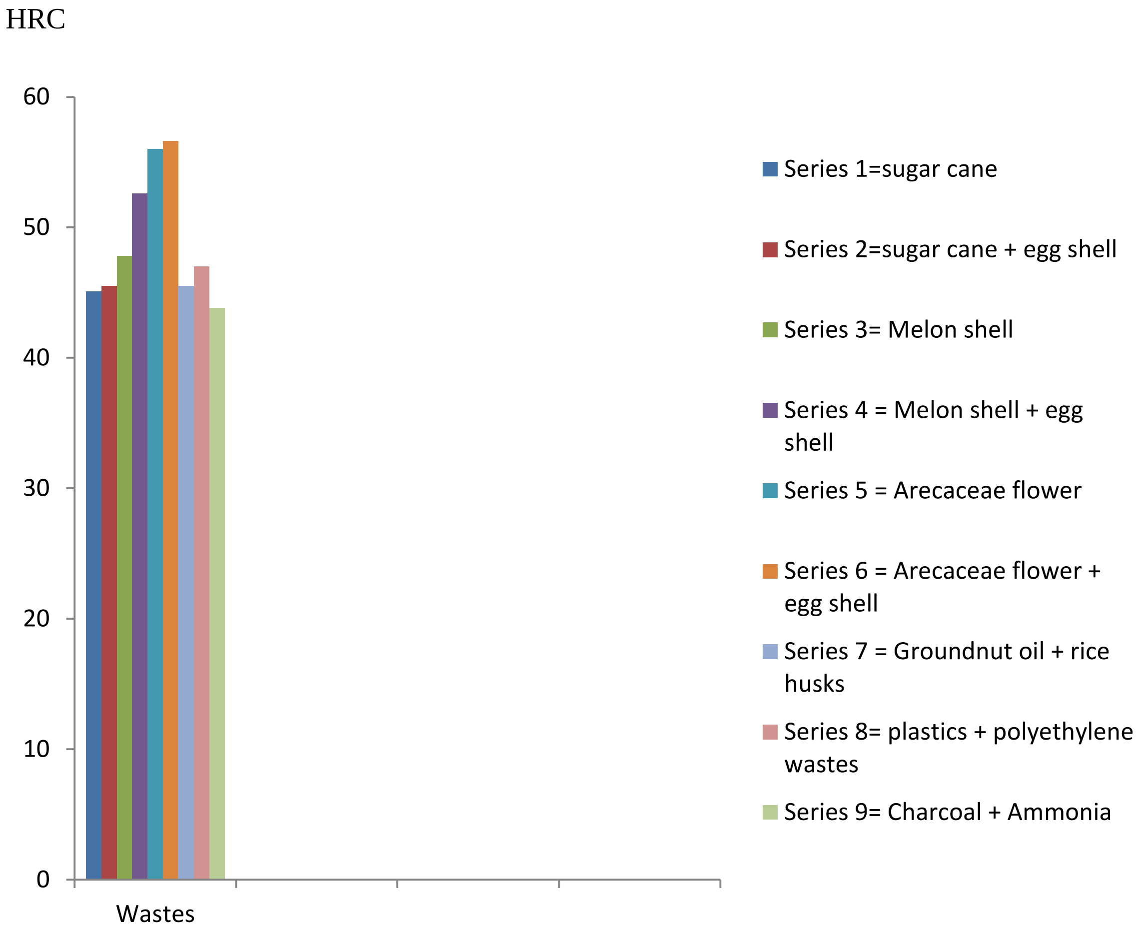

Fig. 1. Shows the Hardness values Produced on Mild Steel by the various Wastes used as Casehardening Material (a reflection of the carbon potential of the waste materials).

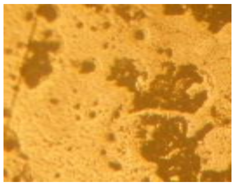

Plate 1: Microstructure of the Mild Steel after treatment with Arecaceae Flower Droppings with dark phases of martensite and varying degrees of carbide, obviously indicating increased carbon content at the surface,(2% nital etched 100 x).

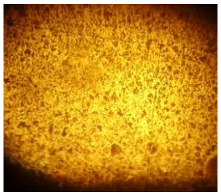

Plate 2. Microstructure of the untreated Steel with a pearlite Structure in a Ferritic Matrix,(2% nital etched 100x).

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