# Investigation of Paste-Based Organic Carbonitriding for Mild Steel Surface Hardening

**K Mohammed Umar**

Postgraduate Student (M.Tech), Department of Mechanical Engineering, Rao Bahadur Y. Mahabaleswarappa Engineering College (RYMEC), Ballari, Karnataka, India

**Abstract**

In this work, the surface hardening of mild steel has been performed with three different organic paste compositions added externally and heat treated (~950 °C bright red heat) in blacksmith furnace. In order to harden the mild steel specimens with paste compositions, three different paste compositions have been used as follows; Case 1: sugar (40%), urea (40%), eggshell powder (20%) and flour; Case 2: charcoal (40%), urea (40%), eggshell powder (20%) and flour; Case 3: charcoal (70%), salt (30%) and flour. The paste composition has been applied to mild steel specimens with an even amount, sealed with clay and heat treated for 30 minutes with subsequent water quenching. The hardness of the work has been measured with Rockwell hardness testing machine and at least 3 readings have been obtained for each case and the average value has been calculated. The hardness values of the work have been increased in the order of Case 2: (35.6 HRC), due to both carbon and nitrogen diffusion from charcoal and urea, probably hard carbonitride phase formation; Case 3: (30.8 HRC), where hardness increment has been mostly due to carburization; and Case 1: (19.8 HRC), where uptake of nitrogen has been limited and no carbonitriding has been observed. In this way, it has been shown that the use of combined carbon nitrogen sources may lead to greater hardness.

**Keywords:** Surface hardening, paste, Mild steel, Pack Carbonitriding.

## 1. Introduction

Mild steel garners a near-universal usage in manufacturing and fabrication industries because of its affordability, ease of fabrication, weldability, and modest mechanical properties for diverse applications [1] Yet, its limiting bearing upon hardness and wear resistance causes it to bear abysmal performance in the presence of high friction, abrasion, or contact fatigue [1,2]. Hence, many surface hardening methods such as carburizing, carbonitriding, nitriding, and induction hardening have been applied to improve the surface characteristics of mild steel while permitting it to retain a tough and ductile core [1,2]. The carbonitriding process is mainly achieved by the diffusion of carbon and nitrogen into the steel surface at elevated temperature to form hard carbides and nitrides that further enhance wear resistance and fatigue strength of the steel [1,2]. This was mostly done by using a gaseous or liquid medium containing toxic cyanide salts, an issue that urgently calls for the search for greener alternatives [3]. Hence, the search for safer, cheaper, and environmentally-friendly alternatives. Prior research has looked into organic and agro waste materials as alternative carbonaceous and nitrogenous substances being utilized for surface hardening of materials.[4] considered powders derived from eggshells and palm kernel shells for the purpose of carburization, whereas [5] contended with sugarcane bagasse and coconut shell charcoal for mild steel carburization. Although these studies showed a promising increase in hardness, most of these act either towards carbon enrichment (carburizing) or towards nitrogen enrichment (nitriding) and have very little contribution towards paste-based carbonitriding using organic waste mixtures. The research gap here lies in the lack of systematic studies on paste-based carbonitriding processes involving both carbon rich and nitrogen rich organic wastes under controlled conditions. In addition, very little is understood on how different organic compositions especially those involving urea, eggshell, sugar, and charcoal affect the hardness of mild steel as compared to the usual toxic process. While low-temperature nitrocarburizing studies (e.g., Illing et al.[1]) have looked at stainless steels to preserve corrosion resistance, the present study covers mild steel, where high-temperature treatment (~950 °C) can be carried out with ease and choice. This allows rapid carbon and nitrogen diffusion within 30–40 minutes, producing carbides and nitrides that improve surface hardness without the extended processing times required for stainless steel. This study is undertaken to bridge the gap by experimenting on the surface hardening of mild steel in three different organic paste compositions, prepared from locally available agro waste materials, applied externally, sealed with clay, and heated in a furnace for 30 min at 950 °C. The objectives are to (1) observe the hardness on the surface (2) compare the performance of differing organic compositions, and (3) show the environmentally benign and cheap alternative to the classical carbonitriding processes. This method should not only help small workshops and rural industries but can be an alternative fastening aim of sustainable manufacture.

**TABLE 1**
**CHEMICAL COMPOSITION OF MILD STEEL**

| C | Si | Mn | P | Cr | Ni | Cu | Al | Mo | S | Fe | **Element** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.13% | 0.03% | 0.5% | 0.03% | 0.2% | 0.2% | 0.09% | 0.02% | 0.02% | 0.02% | Balance | **%** |

## 2.Apparatus and Methods

### 2.1 Apparatus

The equipment used for the research are the following :Blacksmith Furnace, Quenching bath, tongs, hacksaw fixed frame with blade, Industrial digital thermometer, hand blower, Clay, Nital solution and Rockwell hardness testing machine.

### 2.2 Methods

#### 2.2.1Material preparation

The mild steel specimens used for the study were having been obtained from Smt. Vidyaranya ITI College at Hosapete, Vijayanagar District. Eggshells were picked up from a particular eggshell stall. Charcoal, urea, sugar, and flour served as the pastes. Mild steel rods of dimensions 8mm × 20mm and rectangular specimens of dimensions 20 mm × 20 mm × 9mm were first cleaned with acetone and washed with water to remove any dirt on their surface; they were then dried with hot air from a hand blower. Three compositions of paste had been prepared for hardening purposes. Case 1 had a composition with sugar 40%, urea 40%, and eggshells 20% by weight. Case 2 had charcoal in place of sugar, but urea and eggshells remained the same percentage by weight. The paste composition of Case 3 comprised charcoal 70% and salt 30% by weight. The binder used for all paste compositions was flour, with varying amounts of water poured in to obtain the paste. Each paste was then applied on mild steel specimens for surface hardness and dried. After drying, an obstacle clay covering was placed on the specimens to prevent them from exposure to the environment and avoid the opening effect during heat treatment, as shown in Figure 1.

**2.2.2 Pack Carbonitriding process**

Pack carburizing was applied to Case 3-type specimens, while pack carbonitriding was performed on Case 1- and Case 2-type specimens. The specimens covered with clay were heated up to the temperature of 950 °C, and the heating duration was 30 minutes. Heating was done in a coal-fueled blacksmith furnace as depicted in Figure 2. Due to the absence of any temperature measurement system inside the furnace, it was decided to measure the external temperature of the furnace using an industrial digital thermometer. Immediately upon removal from the furnace, care was taken to break off the clay cover with the use of a hammer, and thereafter, the specimens were subjected to water quenching. This rapid quenching preserved the hardened surface, attaining the required surface hardness while avoiding any undesired temperature drops throughout the cooling process. Figures 3 & 4 show the carbonitride and carburizing specimen, respectively.

**2.2.3 Hardness profile**

The hardness profiles of the test samples were checked using a Rockwell hardness testing machine. For the experiments, Rockwell C scale hardness readings were taken. The following description tells how the specimen was tested under a Rockwell hardness testing machine (Model RABI, S.No SN5421) of Saroj Engg. Udyog Pvt. Ltd., as shown in Figure 5. The readings were taken on the HRC scale in accordance with ASTM E18. The brale (120-degree diamond cone) was only to be seated with a minor load of 10 kg (98.7 N). The application of the major load of 150 kg (1471 N) was then performed onto the indentation. Each specimen was indented three times, in cases one, two, and three, and the means were calculated for hardness.

**2.2.4 Microstructure examination**

A treated specimen and an untreated mild steel sample underwent cutting and polishing operations followed by emery paper grinding from 320 to 1200 grit levels. The specimens advanced to the pre-polishing disk which featured a coating of one-micron alumina powder paste. The specimens underwent final polishing on finishing disc using 0.5 mm alumina paste before being washed and dried using a hand blower. The polished surface required etching with 2% nital (98 mL ethanol + 2 mL nitric acid) for 5-10 seconds in order to reveal the microstructure. The specimens were taken to the microscope after which the microstructure was both studied and captured.

**3 Result and discussion**

Table 2 displays the experimental results from hardness testing of three paste formulations through three replicate measurements which determined the average hardness values. The mild steel specimens contained specific compositions which are detailed in Table 1. The hardness measurements used a Rockwell hardness tester machine equipped with a diamond cone indenter (HRC scale) to achieve precise and uniform results. The treatment process used a blacksmith furnace to apply paste mixtures on mild steel specimens which were sealed with clay before heating at 950 °C for 30 minutes followed by water quenching. Nital solution was applied to show the hardened surface layer which demonstrated the diffusion of carbon and nitrogen into the substrate. The mean hardness results in Table 2 indicate that Case 2 (40% charcoal + 40% urea + 20% Eggshell) generated the highest value at 35.6 HRC while Case

3 (70% charcoal + 30% salt) followed closely at 30.8 HRC and Case 1 (40% refined sugar + 40% urea + 20% eggshell) registered the lowest value at 19.8 HRC. The bar chart in Figure 6 illustrates the distinct hardness values for three cases while showing a substantial performance difference between nitrogen-rich pastes (Cases 1 and 2) and the nitrogen-free composition (Case 3). The main contribution of nitrogen together with carbon donors leads to improved hardness. The observation matches previous studies [6,7] which showed that nitrogen-rich compounds like urea when added to carbonaceous media enhance surface hardness through carbonitride formation. During heating at 950 °C under clay-sealed conditions the carbon-rich materials (charcoal, sugar) broke down to produce carbon monoxide (CO) and fresh carbon (C) which penetrated the steel surface to create hard carbides ($Fe_3C$). The thermal breakdown of urea-containing pastes (Cases 1 and 2) produced $NH_3$ and HNCO which decomposed into N and $H_2$. The nitrogen atoms penetrated the steel lattice structure to create iron nitrides ($Fe_4N$, $Fe_{2-3}N$) and carbonitrides. The addition of eggshell powder ($CaCO_3$) in the mixture triggered localized $CO_2$ release that activated surface diffusion processes and carbon dioxide reacted with excess carbon to regenerate CO, thus sustaining the carburizing atmosphere[6]. A hardened surface emerges from the combined actions of carbon and nitrogen diffusion into the material. The outcome of comparing Composition with cyanide and high energy consumption shows [1,3] toxic chemicals and large energy requirements. The organic material like charcoal, eggshell powder, urea it can be observed that the best performing composition occurs without toxic chemicals. The best composition case 2 produces a surface hardness measurement of 35.6 HRC. The composition is 40% charcoal, 40% urea, 20% eggshell powder. The surface hardness measurement for case 3 stands at 30.8 HRC. case 1 has a surface hardness measurement of 19.8 HRC. All these are composition without toxic chemical. The application impact shows that this treatment enables mild steel to resist wear when used as a moving part in machines [8,9] while the time increases. Carbonitriding compounds which lack harmful chemicals are unnecessary for creating quality cases on mild steel according to the study results. The above evidence demonstrates that compounds without toxic chemicals achieved better results than those containing them. The desired outcome was reached within half an hour. The carbonitriding conditions at 950°C were identical across all composition samples during the processing time of 30 minutes. At this temperature steel transforms into austenite that contains FCC structure which permits carbon atoms to occupy interstitial spaces. The carbon potential of charcoal & sugar which supplied nascent carbon to create the case depth appears favorable since carburization occurred. Multiple researchers have investigated this phenomenon [9,10]. The energizers achieve this by elevating the carbon potential within the carbonitriding composition. Multiple researchers together with authors have proposed this mechanism of energizers during carbonitriding processing [6,8,11]. The microstructure analysis of treated sample reveals hard carbide formations which emerged during the 950°C thermal cycle as presented in Figure 7 and Figure 8. The untreated sample maintains its original ferrite pearlite microstructure without any modifications thereby proving that the hardness changes are caused by the applied treatment. These results present a ready comparison against those obtained by Adedipe et al. (2023) and Illing et al. (2021). Adedipe et al. (2023) reviewed the application of agricultural and organic wastes such as eggshells, coconut, and palm kernel shells as energizers in steel carburization, in view of their ability to build up hardness as well as to serve an environmentally friendly alternative to conventional chemical additives. In keeping with this view, this study shows that a paste mixture consisting of eggshell, charcoal, sugar, and urea can impart a hardness of 35.6 HRC on low-carbon steel in 30 minutes of treatment, therefore bearing an encouraging testimony to the practicability and efficiency of organic waste carburization. Conversely, Illing et al. (2021) investigated a low-temperature carburizing treatment via

reagent pyrolysis in the closed vessel, as applied to the case-hardening of austenitic stainless steels, with a view to reducing thermal loads and distortion arising from the treatment. A different steel and a different process design notwithstanding, it is a parallel manifestation of the worldwide trend on sustainable and innovative case-hardening practice.

**TABLE 2: Hardness Data of mild steel**

| Case No | Paste Composition | Percentage Composition | Reading 1 (HRC) | Reading 2 (HRC) | Reading 3 (HRC) | Average Hardness (HRC) |
|---|---|---|---|---|---|---|
| **0** | Untreated Mild Steel | – | 10.0 | 12.0 | 11.5 | 11.2 |
| **1** | Sugar + Urea + Eggshell | 40 – 40 – 20 | 19.0 | 19.8 | 20.5 | 19.8 |
| **2** | Charcoal + Urea + Eggshell | 40 – 40 – 20 | 35.5 | 35.0 | 36.2 | 35.6 |
| **3** | Charcoal + Salt | 70 – 30 | 30.0 | 31.0 | 31.3 | 30.8 |

**Figure 1: Mild steel specimen coated with organic paste and sealed with clay before heat treatment.**

Figure 2: Coal-fueled blacksmith furnace used for paste-based surface hardening at ~950 °C.

**Figure 3: Specimen after paste carbonitriding treatment (Charcoal + Urea + Eggshell).**

**Figure 4: Specimen after paste carburizing treatment (Charcoal + Salt).**

**Figure 5: Rockwell hardness testing machine (Model RABI, S.No SN5421) used for hardness evaluation.**


**Figure 6: The bar chart showing Average hardness values (HRC) of untreated and treated mild steel for the three paste compositions.**

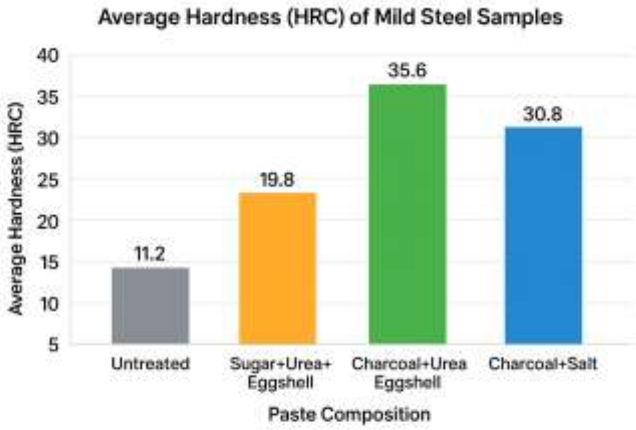



**Figure 7: Microstructure of carbonitrided mild steel (Charcoal + Urea + Eggshell paste) with dark phase of martensite and varying degree of carbide indicating increased carbon /nitrogen content at the surfaces (2% nital etched solution 120 x)**

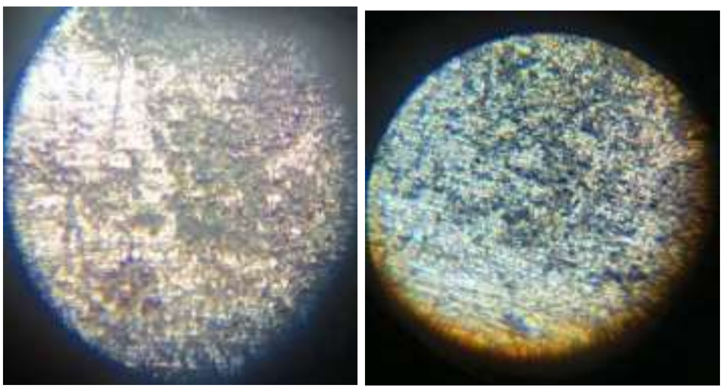
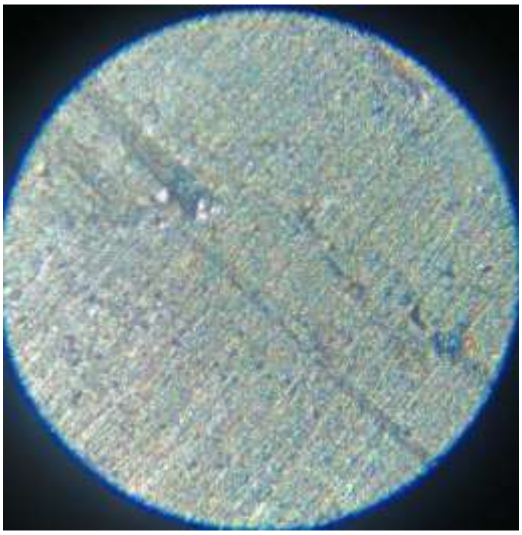


**Figure 8: Microstructure of untreated mild steel showing no dark phase of martensite indicating no carbon content at the surfaces (etched with 2% nital solution) (120X).**



## 4. Conclusion

The research proves paste-based surface hardening which uses organic materials with energizer creates substantial improvements in mild steel hardness thus serving as an ecological replacement to cyanide-based and high-energy industrial methods. The Charcoal + Urea + Eggshell mixture produced the maximum average hardness of 39.5 HRC which demonstrated the best carbon and nitrogen diffusion properties during the tested conditions. The Sugar + Urea + Eggshell mixture showed the lowest hardness value of 20.7 HRC during the current testing period but its composition shows potential since sugar combustion produces clean carbon monoxide which may produce deeper case depths with longer processing times. The findings demonstrate that organic waste-derived carburizing and carbonitriding agents can enable economical and environmentally friendly surface hardening methods for small- and medium-scale industrial operations. The upcoming research will examine the effects of doubling the processing time to 120 minutes to assess how this affects case depth and hardness. The Sugar + Urea + Eggshell mixture will undergo re-evaluation during prolonged processing times to establish if its results improve enough to match or exceed other mixtures.

## Reference

1. Totten, G.E., (2006). Steel Heat Treatment Handbook. CRC Press.
2. Callister, W. D., & Rethwisch, D. G. (2018). Materials Science and Engineering: An Introduction (10th ed.). Wiley.
3. Totten, G. E., & MacKenzie, D. S. (2003). Handbook of Aluminum: Vol. 1, Physical Metallurgy and Processes. CRC Press.
4. Oladele, I. O., & Akinlabi, E. T. (2020). Utilization of eggshells and other biowastes for engineering applications: A review. Cleaner Engineering and Technology, 1, 100023.
5. Oladele, I. O., & Akinlabi, E. T. (2019). Biowaste materials for surface engineering and metal treatment: A review. Journal of Cleaner Production, 230, 1176–1191
6. Ihom, A.P., Nyior, G.B., & Offiong, A. (2012). The potentials of waste organic materials for surface hardness improvement of mild steel. International Journal of Scientific & Engineering Research, 4(5), 1366–1372.

7. Puspitasari, P., Ardhyananta, H., & Triwikantoro. (2017). The effect of urea addition on hardness in carbonitriding process. IOP Conference Series: Materials Science and Engineering, 202(1), 012034.
8. Ihom, A.P. (1991). Case Hardening of Mild steel using Cowbones, B.Eng Degree thesis submitted to Department of Materials and metallurgical engineering, University of Jos 1991, 1-35
9. Azoro, K.U. (2017). Production of Casehardening Compound for Surface Treatment of Mild Steel for Mechanical Property Improvement, M.Eng. Dissertation in the Department of Mechanical and Aerospace Engineering, University of Uyo-Nigeria
10. Aramide, F. O., Ibitoye S. A. and Oladele I. O. (2009), Effects of Carburizing Time and Temperature on the Mechanical Properties of Carburized Mild Steel using Activated Charcoal as Carburizer, Materials Research Journal 12(4): pp 483 – 487. Accessed on 25th August, 2016 http://www.scieio.br.com
11. Asuquo, L. O and Ihom, A. P (2013), Variation of Effective Case Depth with Holding Time of Mild Steel using Various Carburizing Compound, International Journal of Metal and Steel Research Technology 1: pp 12-18
12. Illing, R., Böttger, A. J., & Mittemeijer, E. J. (2021). Solid-state nitrocarburising of austenitic stainless steel using solid urea as nitrogen source. Metals, 11(10), 1651. https://doi.org/10.3390/met1110165
13. Adedipe, O., Medupin, R. O., Yoro, K. O., Dauda, E. T., Aigbodion, V. S., Agbo, N. A.,Oyeladun, O. W. A., Mokwa, J. B., Lawal, S. A., Eterigho-Ikelegbe, O., & Sadare, O. O. (2023). Sustainable carburization of low carbon steel using organic additives: A review. Sustainable Materials and Technologies, 38, e00723. https://doi.org/10.1016/j.susmat.2023.e00723