8.8
Bringing back the shine to copper

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Overview

This unit uses the context of cleaning of metal surfaces to learn about the properties of materials. One of the common metals that students come across in utensils, currency coins, statues, wires, etc., is copper. The pure copper surfaces of such objects often turn brown, black, green, or dull on exposure to air and humidity for two to three days. We use the word "tarnish" to describe this effect. We also experience that simply washing with water or wiping with cloth does not remove the tarnish or dullness, or bring back the shine. This indicates that the dullness-causing substances are strongly attached to the surface and are not dust-like particles sitting on the surface. For cleaning such surfaces, we require specific cleaning agents. This unit explores the acidic/basic nature of various commonly used utensil-cleaning agents, and identifies the cleaning agents appropriate for copper. It further helps us understand the role of some physical and chemical processes in cleaning.

This Learning Unit has four experimental tasks. In task 1, students try to recollect copper objects they have seen or used. Then they take a copper item and use a sand paper to scrub off the tarnish layer to see the colour of pure copper. They *re-expose* it to air to allow the tarnish to develop again. This part is important as it helps them to differentiate the tarnished surface from that of clean copper, and to know that tarnishing is a *natural transformation of copper surfaces* and *not some dust-like impurities* that deposit on the surface from the atmosphere.

Minimum time required

Four sessions of 40 minutes each

Type of Learning Unit

Classroom and laboratory

Task 2 involves observing the changes on the copper surface after rubbing it with different solid cleaning agents. Task 3 involves observing the changes on the copper surface after treatment with different liquid and solid cleaning agents in presence of water. In task 4, students explore the acidic/basic nature of the cleaning agents using litmus papers (red and blue) or turmeric paper (or turmeric powder). The acidic/basic properties of the agents are correlated with their cleaning action on the copper items.

Unit-specific objectives

For students of Class 8, cleaning of metal surfaces can be a good context to understand the following chemistry-relevant aspects:

- To explore the process of cleaning of surfaces, and understand when a cleaning action is chemical in nature (involving transformation of substances), and when it is physical (caused by rubbing/abrasion, driven by friction)
- To differentiate between the cleaning action of substances that are acidic and basic in nature
- To identify the acid/base nature of cleaning substances used in our households and the relevance of this with respect to copper surfaces
- To decide what kind of food can be stored in containers made of copper

Links to curriculum

Relates to chapters on "Metals and Non-metals" and "Friction" in Class 8 NCERT textbook. The unit also connects to concepts of "Acids, Bases, and Salts" and "Physical and Chemical Changes" in Class 7 NCERT textbook. Tarnishing of material surfaces is also related to atmospheric gases and the chapter on Air Pollution.

Introduction

Copper has been a very important metal in the evolution of human civilisation. In history books, we have read that extraction and use of metals led to the end of Stone Age. Use of metal tools started with copper from roughly 5000 BC. The use of copper was known in almost all sites of ancient civilizations like the Egyptian, Chinese, Mesopotamian, Native American, and Indian. In India, several ancient copper tools, coins, and weapons have been found, which tell us about the flourishing copper industry

in ancient India. Some notable examples are the hoards found in the Gungeria village (Madhya Pradesh), the huge copper statue of Buddha discovered in Sultanganj (Bihar) (dated between 500 and 700 CE) and the copper plates of Kalachuri dynasty (12th century CE, Karnataka). The modern era of copper industry in India started in 1967 with the formation of Hindustan Copper Limited by the Government of India. Many regions of India have deposits of copper minerals, from where it is mined.

Image 1: *Household copper vessels*

Today copper finds its uses in telecommunication, electrical wiring, transport, utensils, construction, etc. In our homes, copper objects are used as wires, utensils for storing water and for eating, etc. However, due to a particular problem with copper, its use has been decreasing in our lives. This unit relates to the problem of copper that has caused the decline in use.

Image 2: *Statue of Buddha discovered in Sultanganj, Bihar (left). Copper plates of Kalachuri dynasty (right)*

Task 1: Recollecting what we know

Q1. What copper objects have you seen in your home and your surroundings?

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Q2.What are the colours of their surface?

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Materials

Small-sized tarnished or dull copper items (plates/strips), vinegar, baking soda, lemon juice, common salt, tamarind (*imli*) juice, liquid detergent, detergent powder, coal or wood ash, curd, and sand paper (zero grade).

In countries like India, with a hot and humid climate, copper objects get easily tarnished, making them look dull and unattractive. Pollutants in the air also increase the tarnishing. Surface tarnish leads to large losses in business for the traders and the economy. Therefore, cleaning of the surface tarnish of copper (and other metals) is a need in many professions. In this Learning Unit, we will try to clean such dull/tarnished copper utensils using some common household materials, and learn the science behind this process.

Take a small copper object or strip.

Q3. What is the colour of its surface?

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Rub the surface using sand paper (zero grade).

Q4. What is the colour of its surface now? Has it changed on rubbing with sand paper? What property of sand paper is responsible for it?

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The colour changes because the rough surface of sand paper removes small particles of surface material. If the tarnish layer is thin, then the underlying metal is soon exposed.

Q5. Is any copper lost in this process?

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Answer: Yes, it is scraped away by the sand paper. One can observe it in the scraping dust.

Now, keep this shining copper object near a sink or in a chemistry laboratory near where chemicals are stored. After two-three days, you will use this in task 2.

Q6. What substances have you seen being used for the cleaning of copper objects/utensils?

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Q7. Table 1 lists some substances. Before performing any trial, guess which of these substances can clean the tarnished copper objects and why (because it dissolves many impurities/has lot of solid particles/is soapy to touch/produces a lot of foam/any other reason)?

Substance	Will it clean? (Yes/No)	Why do you think it will clean copper?
Vinegar		
Baking soda		
Lemon juice		
Common salt		
Tamarind juice		
Liquid detergent		
Detergent powder		
Coal or wood ash		
Curd		

Table 1 *Predicting the action of different substances on copper*

The question 7 above must be answered before performing any trials. This question requires students to think of what properties of a substance can make it a good cleaning material for an object or material. For example, detergents can solubilise many kinds of grease and dirt particles, and hence are used for washing. Water can wet or suspend many substances and hence is used to clean many objects.

Now, let us find out whether our guesses are correct. The following tasks (Tasks 2 and 3) can be performed in groups of 3-4 students.

Task 2: The action of solid cleaning substances on tarnished copper

Q1. After two-three days, did you observe any change in the surface of the copper object you cleaned in task 1?

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Materials

Tarnished copper plates/strips, hand gloves, used toothbrush, watch glass/ saucer, droppers and small spoons/spatulas, water. Three or four of these cleaning agents: Talcum powder, baking soda, detergent powder, sand (or white rangoli powder), dry soil, common salt, ash.

Approach for tasks 2-4: Here we recommend a list of substances that are commonly used for cleaning: vinegar, lemon juice, baking soda/powder, coal ash, wood ash, detergent powder for utensils, common salt, curd and tamarind (imli) juice. Small saucers/plates/test tubes/watch glass can be used to hold the cleaning substances. The list includes acidic, basic and neutral substances. Teachers may arrange the substances as per their availability. It will be helpful if at least four to five substances (containing at least one acidic, basic, and neutral substance) are used in the tasks. The typical composition of the substances mentioned above is given in Appendix A. For rubbing the surfaces, used tooth brushes can be used.

Planning the task distribution (if less time is available)

In a science circle of, say, 30 students, make two groups of fifteen students each. Group 1 can be assigned the acidity/ basicity test of the cleaning susbtances whereas group 2 can perform the cleaning tests. Within each group, smaller groups or pairs of students can be given three to four cleaning substances to test for their acidic, basic, or neutral nature. Similarly for group 2, small groups or pairs can be given at least three to four cleaning substances to test for their action on the tarnished copper items. Ideally, each small group or pair should get an acidic, a basic, and a neutral cleaning substance for performing the tests as per their availability.

Safety Measures!

DOS

✓ Use hand gloves to cover hands when performing the task.

✓ Use the cleaning substances carefully and in the amount mentioned in the instruction.

✓ Use only toothbrushes (or similar scrubbing tool) for rubbing.

✓ Make sure to wash hands properly with water and soap after performing the activities.

✓ If any student's hand is itching, wash it with water immediately.

DON'TS

× Make sure you do not spill the cleaning agents on the skin, clothes, or on the table.

× Do not touch any part of your eyes, lips, mouth or nose, when using the cleaning agents.

Procedure

Add 1/3 of a small teaspoon (approx. 0.5 g) of substance to a small area on the plate/strip and rub the substance gently using a toothbrush for a minute.

Note: At a time, apply only a single cleaning substance on dark/tarnished spots of the copper surface. If there is no change, the same plate/strip can be cleaned with a tissue paper/cloth and then washed with a little water to remove the previous cleaning agent before performing the next test. If there is a change, then another plate/strip or unused area of the same plate should be used to perform the next test. After performing a test, the tooth brush should be kept dipped in water and then dried before using it again, to prevent cross contamination.

Solid cleaning agent	Observations (Cleaned/Not cleaned/Scratches formed/Other)

Table 2 *Results of using (dry) solid cleaning agents on copper surface*

Q2. Which of the solid cleaning agents removed the tarnish?

Q3. Did you observe any scratches on the tarnished surface for any of the cleaning agents? What do the scratches tell you about the nature of the cleaning agent?

Q4. Is rubbing of a solid substance on a copper surface a physical or a chemical action?

Task 3: The action of liquid cleaning agents on tarnished copper

Each group may take the solid agents used in task 2 and prepare their pastes by adding a few drops of water to each. In addition, take two to three cleaning agents from this list: vinegar, lemon juice, curd, tamarind (imli) juice.

Take some water, and the various liquid cleaning agents in watch glasses or in saucers. Dip the tarnished copper object in the cleaning substance and observe for 2-3 minutes. If no change is observed on the surface, then use the toothbrush

Materials

Task 3: Solid cleaning agents used in Task 2, used toothbrush, watch glass/saucer and any two or three cleaning agents from this list: vinegar, lemon juice, curd, tamarind (*imli*) juice.

to gently rub the copper surface (clean the brush under water after every use). Note down your observations (colour change/ evolution of gas/any smell) in the table given below.

Note: If the copper item is big, then a small area can be used for testing. In that case, about 0.2 mL or 5 drops of the cleaning agent can be applied on the copper surface for the testing. If no change is observed, then the same copper object can be used for trying the next cleaning agent after cleaning the area with water, else another object or an unused area of the object may be used.

Cleaning agent	Observations	
	Dipping the surface in the liquid/solid-water paste	Rubbing the surface with liquid/paste and toothbrush
Water		

Table 3 *Results of using cleaning agents (with water) on copper surface*

Typical observations obtained for the action of cleaning substances are shown below.

Cleaning agent	Observations	
	Dipping the surface in the liquid/solid-water paste	Rubbing the surface with liquid/paste and toothbrush
Water	No effect	No effect
Vinegar	Cleaned	Cleaned
Baking soda	No effect	No effect
Lemon juice	Cleaned	Cleaned
Common salt	No effect	Slightly cleaned

Tamarind juice	Cleaned	Cleaned
Ash	Partly cleaned	Partly cleaned
Curd	Slightly cleaned	Slightly cleaned
Detergent powder	No effect	No effect

Table T1

Please note that the table contains results of one set of trials. Your students' findings may vary depending on the purity of copper in the object, nature of tarnish layer, and also the source of cleaning agent. For example, freshly prepared curd is not too sour and may not show the same effect as some old curd which may be very sour.

Q1. From your observations, which of the cleaning agents cleaned your plates/wire strips?

Q2. To clean the copper surfaces, was it necessary to rub the surface in all cases?

Q3. Which of these cases of cleaning the copper surface involved a chemical change?

If a cleaning agent cleaned the surface without any physical effort (i.e., just by keeping it in contact with the surface), then it can be called a chemical change. Thus, students should check — in which cases the surface was cleaned without any effort.

Task 4: The acidity/basicity of the cleaning agents

Let us see if the acidic or basic nature of a cleaning agent affects its cleaning action for copper tarnish. To understand this, we need to know the nature of the cleaning agents that cleaned the surface without need for a physical action and compare it to substances that did not. We will check this with the help of indicators.

Students must take only one cleaning substance at a time to determine the (acidic/basic) nature. They must wash hands properly before using the next cleaning agent to prevent cross contamination.

If red litmus is not available, then blue litmus paper can be converted to red by dipping in dilute hydrochloric acid and then quickly rinsing with water. Similarly a red litmus can be converted to blue litmus by dipping in sodium carbonate or sodium hydroxide solution and then quickly rinsing with water.

Materials

Three to four of each of the solid and liquid cleaning agents (as used in tasks 2 and 3), litmus papers (red and blue), turmeric powder or turmeric paper, watch glass/ saucer), droppers, and small spoons/spatula.

For solid cleaning agents, take 1/3rd of a small teaspoon or ice cream spoon (approx. 0.5 g) of the cleaning agent in a watch glass or in a saucer, and add 2 mL of water to it. For liquid cleaning agents, take about 5-6 drops of the liquid on a watch glass (or in a saucer). Dip the blue and red litmus papers one after another in the liquid cleaning agent. Note the colour change of litmus papers in the observation table. If liquid indicators are available, then add 2 drops of one of these in the cleaning solution in the watch glass. Note the colour change of the indicator in an observation table.

Note: Wash your hands thoroughly with water before and after using each indicator.

Cleaning agent	Red litmus	Blue litmus	Turmeric paper/ other indicator	Conclusion: Nature of cleaning agent (acidic/ basic/ neutral)
Lemon juice				

Table 4 *Acidic/basic nature of cleaning agents*

Q1. Based on your observations in tasks 2, 3, and 4, can you say if the acidic/basic/neutral nature of the cleaning agent has some role in the cleaning of the tarnished copper utensil/wire strips?

Yes ☐ No ☐

Q2. What can you conclude about the cleaning mechanism of the agents based on all the tasks?

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Students are initially likely to conclude that cleaning is due to a chemical reaction between acidic substances and the tarnish on the surface. However, teachers may ask why some parts of the copper seem clean due to salt, although salt is not acidic. The answer lies in the fact that the rubbing action with salt in the presence of some water cleans the copper surface. It follows that students should think about the role of rubbing in cleaning. During rubbing, friction between the particles of the solid cleaning agent, scrubber and the tarnished copper surface might result in removal of particles of tarnish layer, and even some particles of copper metal itself. In addition, salt has a complex chemical reaction with copper which further helps in cleaning of surface. Other substances such as ash or sand when scrubbed hard will also clean the surface, which will be largely due to physical process.

Q3. Based on the above tests, can you say whether the nature of the tarnish in the copper utensil is acidic/basic/neutral? Give reasons for your answer.

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Q4. What kind of waste is produced in cleaning copper by the agents you used? Is any of this harmful to nature?

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This question is intended to raise consciousness among students about the waste we produce while cleaning! So, encourage students to think about what is being thrown away. What goes into the drain besides water? What happened during scrubbing and where did the particles go ? We used cleaning agents. Are there packets of cleaning substances also that we threw away/discarded ?

Q5. Did you have any unusual findings or observations in the above three tasks ?

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Here students may write new observations which differ from their current knowledge of the subject.

Q6. Which of the following food substances **cannot** be stored in copper utensils? Why?

Buttermilk, common salt, pickles, tamarind chutney, rice,........

Add a few more food items to this list.

Can be stored	Cannot be stored	Not sure
	Buttermilk	
	Pickles	
Rice grains		

Table 5

Q7. Why do you think the use of copper utensils in households has decreased in our households over the years ?

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Here, students may talk about the price of copper, and its corrosion, which limits the kind of food that can be stored in it. Corrosion also leads to faster loss of metal and thinning of utensil. They may also talk about the availability of cheaper alternative materials for utensils such as steel and plastic, which do not tarnish and also do not react as much with food materials.

Tarnishing has led to discolouration in many historical monuments and artifacts in the world. One of the classic examples of copper tarnishing is of the Statue of Liberty, New York (USA). This statue has a core structure of iron, with copper sheets on the surface. It was gifted by France to USA in the year 1886 and has been an icon of freedom. The statue has long lost its original copper colour and has gained different colours over the decades, presently having a greenish blue colouration on the surface.

It is almost impossible to guess that this statue might be made of copper from its appearance/look.

Image 3 *Statue of Liberty and its transition from the original (an artist's reproduction of how it would have looked like in 1886, left) to its transition state (middle) to the latest image (right)*

Post-task discussion

After performing the tasks, the results of all groups can be written on the blackboard for all the students to refer to. The teacher can initiate a discussion regarding the process of cleaning. Questions like- "What is the process through which these cleaning substances clean ?", "Why did some substances clean the copper surfaces while some did not?", "Are the properties of the cleaning substances different?" can be asked to start the discussion. In general, only the substances that are acidic show positive changes due to chemical action. However, curd, an acidic substance, may not clean the tarnished copper plates. This may happen if that curd has low acidity or high fat content in it.

For ash, the cleaning in general is observed only during scrubbing and not merely on contact. Silica, alumina, and some of the metal salts present in ash are abrasives and remove the stain layers by frictional force. Chemical action, on the other hand, does not require the use of physical force. In a chemical action, the cleaning substance reacts with the stain deposits and dissolves them away slowly. Vinegar/lemon juice removes the green stains on the copper surface (with the evolution of gas as bubbles, which can be seen if observed very carefully).

The agents that are able to chemically clean copper are mostly acidic in nature, which indicates that the tarnish substance is basic in nature. Tarnish substance sometimes reacts with acid, liberating gas, which mostly indicates the presence of carbonate salt. However, in some cases the green stains turn black on adding vinegar/lemon juice and do not get removed.

Note that students may not be able to write the chemical reactions taking place between the acidic substances and the tarnished layer on metal, because it is not a very simple system. In simplistic terms, we can assume that CuO (black coloured layer) or basic $CuCO_3$ (green coloured deposits) get dissolved in acidic substances. This dissolution process is not just an acid-base reaction but also involves complexation of Cu(II) ions with anions present in the acidic substances. Some studies have also shown that cleaning is more effective with NaCl (common salt) because it facilitates formation of Cu(I) ions (Ref. 1). In this task, we have not used common salt in combination with other cleaning substances, because this becomes a more complicated chemical reaction.

However, even without going into these details, this activity is very useful to develop skills of qualitative observations, and of differentiating between changes due to chemical and physical phenomena.

Further extensions/discussions about this unit

If time permits, the following questions may be used for further discussion:

1. Cleaning also produces waste. What is the nature of waste produced during large scale cleaning of metal surfaces in industries ?
2. During the chemical cleaning process, is the tarnished metal removed from the surface (i.e., are we losing metal) ? How can this be found out ?
3. Which method of cleaning the metal is more effective (chemical or physical) ?
4. Which cleaning agent(s) (or class of cleaning agents) is/are more effective ?
5. Traditionally copper vessels, commonly used for cooking, were coated with a layer of tin to prevent tarnishing. This process known as "Kalai' was an art with skills known to few. Are any of the students aware of this ? Can they recall the process used by the artisans if they have seen it ?

Combined effect of common salt and cleaning substances on tarnished copper objects can also be explored.

References

For further reading on cleaning of copper surfaces, the following readings may be helpful. These use copper coins (pennies in the USA) with various cleaning substances.

- Rosenhein, L. D. (2001). The household chemistry of cleaning pennies. *Journal of Chemical Education, 78*(4), p513.
- Cynthia L. B. (2008). *Amazing kitchen chemistry projects: You can build yourself.* Nomad Press.
- O'Hare, M. (2007). *How to fossilise your hamster: And other amazing experiments for the armchair scientists.* Great Britain: Profile Books Ltd.
- Information about historical uses of copper taken from IACS Institutional Repository.

Image sources

- Image 1: (Left) pixabay.com/en/utensils-copper-utensils-cooking1457356/, (Right)- Chitra Joshi (HBCSE) (Creative Commons license).
- Image 2: (Left) https://commons.wikimedia.org/wiki/File:Sultanganj-budda.jpg temple-copper-plates, (Right) www.

archaeology.org/news/591-130220-india-karnataka-temple-copper-plates

- Image 3: Adapted from https://pixabay.com/photos/queen-of-liberty-statue-of-liberty-202218/

Appendix A: Composition of cleaning substances

Cleaning Substance	Main Components	Other Components
Vinegar	5-8 % of aqueous acetic acid	Can vary according to the source and use
Baking soda/powder	Mainly Sodium bicarbonate	Monocalcium phosphate and sodium aluminum sulfate
Lemon juice	Vitamin C (ascorbic acid), citric acid	Carbohydrates, sugars, fibres, fat, protein, other vitamins, minerals like calcium, iron, magnesium, manganese, phosphorous, and zinc
Common salt	Sodium chloride	May also have alumina, silicates, magnesium carbonates, and potassium iodide
Tamarind juice	Vitamin C (ascorbic acid), tartaric acid	Carbohydrates, sugars, fibres, fat, protein, minerals like sodium, potassium, calcium, iron magnesium, copper, selenium, phosphorous, and zinc
Coal ash	Silicates, alumina, oxides of iron	Oxides of sulphur, calcium, magnesium, sodium, and potassium
Wood ash	Calcium oxide / carbonate, phosphates, oxides of iron	Oxides of potassium, manganese, copper, and zinc
Curd	Lactic acid, proteins, calcium	Fats, carbohydrates, vitamins, and salts of sodium, potassium, and magnesium
Detergent powder	Surfactants, phosphates, sodium silicates, sodium carbonate	Bleaching agents, sodium hydroxide, sand, and anti-caking agents

Table T2

Appendix B.

Sample results of various substances on tarnished copper vessels without any scrubbing. Students' results may slightly vary from these depending on the source of cleaning agents. The change in cleaning results with scrubbing may vary significantly depending on the pressure with which scrubbing is done.

Action of dish washing bar

Before After

Action of wood ash

Before After

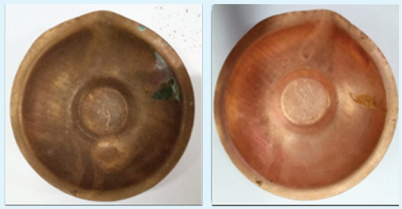
Action of baking soda

Before After

Action of lemon juice

Before After

Action of vinegar



Before After

Action of liquid soap

Before After

Action of curd

Before After

Action of tamarind paste

Before After

Title: Bringing back the shine to copper

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