Introduction

Presently there is a trend towards the use of natural colours throughout the world. Now-a-days, people prefer more usage of natural dyes and colours in food and colouring the textile and other consumer items. All this happened due to the excessive use of synthetic molecules in the last two centuries, which disturbed the eco-systems. Similarly, it is estimated that production of synthetic dyes is around 10,00,000 tones per annum whose production and application release vast amount of waste and unfixed colourant which cause health hazard, pollution and disturb the ecological balance.

As far as natural colours or vegetable dyes are concerned, India had a virtual monopoly in their production and applications. Dyeing and printing was a craft up to the middle of 19th century and India has a very rich tradition of using natural dyes. It is also reported in literature that natural colours extracted from bhesu, palash or tesu flowers [Butea monosperma (Lam.) Kuntze] and turmeric (Curcuma longa Linn.) have been used for playing Holi (festival of colours). After the advent of synthetic dyes in middle of 19th century, natural dyes were forgotten and abandoned as a part of history due to neglect for about 150 years. It is only during the last one and half decade, when concern for environment created an interest in natural dyes, its production and R&D.

Government of Germany was the first to take initiative to put up ban on azo-dyes for manufacturing, dyeing and importing textile and other consumer goods dyed with these dyes. Reference may be made to German Legislation (Consumer Goods Ordinance) w.e.f. January 1, 1995. Netherlands followed with a ban with effect from August 1, 1996 on similar lines. India has also banned the use of specific azo-dyes and under notification “sufficient legal teeth” had been given for taking penal action against those who use these dyes. Reference may be made to clause (d) of sub-section (2) of section six of the Environment (Protection) Act 1986, read with rule 13 of the Environment (Protection) Rules, 1986 w.e.f. June 23, 1997. Certain chemicals e.g. pentachlorophenol, formaldehyde, benzidine, hexachlorobenzene, aldrin, polychlorinated biphenyls etc. and their derived compounds numbering about 118 have already been included in Red-List and banned.

With a view to provide a safe alternative to synthetic-based dry colours, NBRI has developed the process technology for the preparation of Herbal Gulal (dry colour powder) composition using natural dyes and natural ingredients. The technology has already been transferred to a private company (M/s D.M.Herbal, Sakti, Chattissgarh) for its commercial large scale production. The company has started the production of herbal-gulals and the product would be available in the country, in plenty, at the eve of Holi.

Current Status

Dry colours are used world over in various festivals, dances and household decoration; for example, a large amount of dry colours are used in traditional Holi playing and under the present scenario almost 99% of colours used are synthetic dye based. The dry colours (Gulals) available in market are generally of non-standard specifications/parameters and hence their quality is not satisfactory for direct skin and face application. All the blended dry colours (Gulals) available in market for Holi playing are...
synthetic dye based in which clay, sand, dolomite, chalk, starch etc. are used as ingredients. Mica powder is also used in dry Gulal powders, which cause considerable damage to eyes. According to some reports, colours used in Holi contain appreciable amount of toxic and harmful chemicals. The fast colours available at the time of Holi are made from chemicals/dyes which are meant for paint and dyeing. These colours are harmful to skin and eyes. According to the reports of Industrial Toxicology Research Centre, Lucknow, several harmful synthetic dyes have been used for the preparation of colours for Holi purpose. Some of these are as follows:

**Auramine (Yellow colour):** It is a basic or cationic dye which belongs to Diphenylmethane class. There are two important commercial dyes of this class, Auramine O and Auramine G (CI Basic Yellow 2 & 3; CI 41000, CI 41005).

**Malachite Green series (Green colour):** These belong to Triphenylmethane class. Malachite green (CI Basic Green 4; CI 42000) is an important member of the class containing two amino groups, each of which substituted with two methyl groups.

**Rodamine B (Bright reddish violet colour):** It belongs to Xanthene class; CI Basic violet 10; CI 45170. It is also classified as an anionic pigment of the lake type.

**Methyl violet (Violet colour):** These dyes are derived from triphenylmethane or its homologues. Dyes of the methyl violet series (CI Basic Violet; CI 42535) have shades varying from reddish to bluish violet according to degree of substitution.

**Methylene blue (Blue colour):** These series of dyes are analogues of the oxazines, an atom of sulphur replacing oxygen in the heterocyclic ring and are classified as Thiazine dyes. The most important thiazine dye is Methylene blue (CI Basic Blue 9; CI Solvent Blue 8; CI 52015).

**Blends of synthetic dyes:** Various dyes are blended to develop different colours and shades.

As there are no strict regulations, there is very likelihood that some other harmful and banned dyes are being used. The direct application of these dry colours on face and skin often cause eye-irritation, allergies, skin infection and respiratory problems. Moreover after washing, toxic effluents are released which pollute environment and cause health hazard.

**Natural dyes used under the process**

For the preparation of Herbal Gulals numerous safe natural dyes can be used. A brief description of some of natural dyes is presented below:

**Turmeric (Curcuma longa):** It is obtained from the rhizomes of Curcuma longa Linn. syn. C. domestica Valton, family: Zingiberaceae. Its rhizomes are used as spice in foods. It is also used in traditional system of medicine in different herbal formulations. Curcumin being the most famous and brightest of naturally occurring yellow dyes is extracted from the fresh or dry rhizomes. This substantive dye belonging to Diarylmethane group is capable of directly dyeing silk, cotton and wool. India, one of the largest producers with a production rate of 2,50,000 – 3,00,000 tonnes consumes most of this for use as spice and only 1500 -2000 tonnes is

<table>
<thead>
<tr>
<th>Curcumin</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class</td>
<td>Phenalone; Turmeric yellow; Natural yellow 3</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C_{21}H_{20}O_{6}</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>368</td>
</tr>
<tr>
<td>Colour shades</td>
<td>Lemon yellow at pH 3; Orange at pH 10</td>
</tr>
<tr>
<td>Solubility</td>
<td>Oil-soluble</td>
</tr>
<tr>
<td>Absorptivity</td>
<td>E_{1%} = 1607 at 426 nm in ethanol</td>
</tr>
</tbody>
</table>
converted into extract. The curcumin content in turmeric varies a lot depending upon habitat. Generally, it is about 3%. Pure curcumin is not an ideal product for direct use by the food industry since it is insoluble in water and has poor solubility in other solvents. It is usually converted into convenient application form. It is dissolved in food grade solvents and permitted emulsifier. Polysorbate 80 is generally used as an ideal carrier for curcumin. The diluent/emulsifier product contains 4 to 10% curcumin. Oil and starch are also used to prepare curcumin suspensions. Apart from dyeing applications, it possesses antifungal, healing, anti-oxidant, anti-inflammatory, anti-microbial, anti-fatigue, anti-bacterial etc. properties.

**Annatto (Bixa orellana):** The colour is obtained from the seeds of the tropical bush *Bixa orellana*. Major colour constituent: Cis-Bixin and Nor-Bixin. Physical and structural characteristics: Carotenoid; CI Natural 4. The colour is extensively used in dairy products (cheese, cheddar cheese, ice-cream, spreads etc.), flour confectionery (biscuits, ice-cream wafers and snack foods), fish products, sugar confectionery, soft drinks, dry mixes, meat products.

**Indigo (Indigofera species):** Many of the *Indigofera* species, family Fabaceae (Leguminosae), can produce Indigo, but the most significant one is *Indigofera tinctoria*. The colouring matter is present in the leaves of plant in the form of a soluble, colourless glucoside, Indican, a combination of glucose and indoxyl. Indoxyl readily reacts with atmospheric oxygen to form the insoluble pigment indigotine, also known as indigo blue. The whole plant is extracted with water in cement lined tanks and greenish-yellow sap is allowed to ferment. The average yield of indigo is 25% of the total extractable colouring matter.

Indigo, like other vat dyes, is insoluble in water and therefore cannot dye a textile fibre directly. It must be reduced in presence of alkali to its leuco or reduced, soluble form. After the material has been treated in a dye bath, the blue insoluble form is regenerated back by air oxidation. The dye is deposited in the fibre in a fine dispersed state and mechanically held in the fibre matrix. Indigo is one of those few natural dyes, which can dye both animal and vegetable fibres. It is used since ancient time to dye silk, wool and cotton and considered safe. The dye is easily available in market. The cost of the dye varies a lot depending upon the purity and ash content.

**Chlorophyll:** It is a vitally important pigment in nature and present in all plants capable of photosynthesis. In food industry, much effort is put into retaining the chlorophyll naturally present in the green vegetables. However, the addition of chlorophyll as a colour to foodstuffs is very limited, principally because of its poor stability. It degrades easily, particularly in acidic conditions, losing its Mg-ion to yield phaeophytin, which is yellow-brown in colour. Chlorophyll colours tend to be rather dull in appearance and of olive green-brown in colour. It is an oil-soluble colour that can be extracted from a large range of green plant parts. These colours can be standardized using vegetable oils or blending with a food grade solvent or permitted emulsifier to give water miscible form. An extract of chlorophyll will contain approximately 10% of chlorophyll together with other colouring compounds, particularly lutein and carotenes as well as fats, waxes and phospholipids. The replacement of central Mg-ion with Cu produces a more stable complex with greater tinctorial strength. Copperchlorophyllin is permitted as a food colour in many countries.

**Beetroot:** The pigments presenting beetroot are collectively known as betalain and can be divided into two classes, the red betacyanins and yellow betaxanthines; both are water-soluble. It is an excellent source of colour and some varieties
Anthocyanins: The anthocyanins are water-soluble plant pigments, generally occur in the aqueous cell-sap and are responsible for the large variety of colours in flowers, fruits and vegetable: red-violet-blue. The list of sources includes grapes, red and black currants, strawberries, apples, cherries, red cabbage, raspberries etc. Chemically, they are glycosides of flavlium chloride or 2-phenylbenzopyrylium salts; their sugar free pigment is known as anthocyanidines. These are based on six anthocyanidines, namely Pelargonidin, Cyanidin, Delphidin, Peonidin, Malvidin and Hirsudin and sugar moiety present is glucose, galactose, rhamnose or arabinose. Grapes are the single most abundant fruit harvested in the world. The grapes skin left after the contain up to 200mg/100g fresh weight of betacyanins representing 2% of the soluble solid. The beetroot juice is concentrated with sugar, which yields 0.5% betacyanins with 70% sugar. Maltodextrin is also used as carrier. Betanin (C_{26}H_{26}O_{13}; Beet red at pH 5; Red to blue-red; water soluble) is a particular intense colour and is stronger than many synthetic colours. It is used in different food items like ice-cream, yoghurt, dry mixes, sugar confectionery, etc.
extraction of juice has sufficient colour remaining to justify colour extraction. The most prominent is grape skin extract; molecular formula, C_{23}H_{25}O_{12}, molecular weight, 529; red shade at pH 2 and blue-red at 4; water soluble; E_{1%} = 500 at pH 1.5 at λ_{max}, closest to 520 nm. It is used for colouring many food items like soft drinks, dairy products, fruit preserves, sugar confectionery, frozen products, dry mixes, wines, vinegar and desserts.

Cochineal and carmine: Carmine is the aluminium chelate of carminic acid, which is extracted from the dried female coccid insect Dactylopius coccus costa (Coccus cacti Linn.). It provides orange shade at pH 5.5 and purple at pH 7. The water-soluble colour is used in various applications like meat, jams, gelatin dessert, dairy products, flour confectionary, soft drinks etc.

**Lac dye:** It is obtained from the resinous protective secretion of the tiny lac insect, Lacciferidae, which is a pest on a number of plants. The commonest and most widely occurring species of the lac insect in India is Laccifer lacca. It is generally recorded on Indian jujube (Ziziphus mauritiana L.am.), Pigeon pea (Cajanus cajan (Linn.)Millsp.] and Cutch tree (Acacia catechu Willd.). Lac contains a water-soluble dye, laccic acid, and an alkali and ethanol soluble yellow dye, erythro laccin. Laccic acid is a hydroxy anthraquinone carboxylic acid and erythro laccin is tetra hydroxy methyl anthraquinone. In classical methods of dyeing cotton, silk or wool, it is mordanted with alum and myrobalans are used to provide shades and fastness properties.

The principle colour constituents belong to flavonoids (chalcones) class in which butein, buteol etc. are present. For textile dyeing, the colour is extracted in acidic medium and some of the mordants like lodh and myrobalans are used to provide shades and fastness properties.

**Tesu or Keshu dye**

[Butea monosperma (Lam.) Kuntze syn B. frondosa Koenig ex Roxb.]: It is also known as palas, dbak, khara and Flame of the Forest. It bears bunches of large brilliant red flowers during March-April. In olden days, the colour extracted from its flowers has been used for playing Holi and for dyeing clothes to basanti colour during a festival, Basant Panchami. The principle colour constituents belong to flavonoids (chalcones) class in which butein, buteol etc. are present. For textile dyeing, the colour is extracted in acidic medium and some of the mordants like lodh and myrobalans are used to provide shades and fastness properties.

The list of natural dyes is very long and there is scope to use a variety of dyes. Under the present process, natural dyes extracted from Curcuma longa (Curcumin), Bixa orellana (Bixin and Nor-bixin), *Indigofera tinctoria* Linn. (Indigoid), Lac dye from insect Laccifer lacca (Laccaic Acid), Chlorophyll (Chlorophyllin by replacing Mg-ion with Cu) and blends of these dyes have been used for the preparation of dry colour powders. These dyes have been selected considering their easy availability in market, moderate cost and safety aspects as some of these are used in traditional system of medicines and also as food additives.

**Novelty of the process**

Under the process, a safe natural dye or mixture of natural dyes is used; natural dye may be extracted from vegetable/animal sources or may be procured from market. The above procedure is novel as food or pharmaceutical grade natural ingredients are used as bulking agent/filler materials along with food grade vegetable binding and thickening agents. Special attention has been paid towards using soft mordants of Na, K, Ca, Al etc. in safe bio-limits. For the preparation of herbal gulals with any dye, no salts of heavy metal like Cr, Co, Cd, Ni, Pb, etc have been used. The combination provides a powder material having soft and supple touch with good texture,
Manifold option of the procedure

The process provides a wide range of herbal dry colour compositions using different amounts of natural dyes with natural ingredients in different proportions. Different shades of various colours from light, medium or dark could be developed using different amount of dye(s) and mordants. More than 50 shades of herbal **gulals** have already been prepared at NBRI. There is a lot of creativity in using different types/concentrations of dye(s) and fixing agents. Hundreds of shades could be developed. Different natural fragrance viz. rose, sandalwood, jasmine, citronella etc. can also be used depending upon choice and colours of the herbal **gulals**.

**Main advantages of the process**

1. It provides an option to replace synthetic dye based dry colour composition by natural ones, which is safe, stain-free and eco-friendly. Presently, there are no options except to use synthetic based colours.
2. The powder provides a synergistic mixture of coloured dry powder, which has good sticking capacity to skin and can be easily removed by soft mop. The dry colours have cosmetic effect on skin too as they make face feel a bit soft.
3. The people who are scared of celebrating Holi because of the use of toxic synthetic dye based **gulals** which not only damage the skin but cause considerable pain to remove it but now have option to celebrate the festival.
4. The dry coloured powders can be used for cultural dances and making **rangoli** in houses.
5. The raw materials for natural ingredients of food, commercial or pharmaceutical grade are available in market.

**PROCESS TECHNOLOGY FOR THE PREPARATION OF HERBAL GULAL**

- **Dye-yielding raw material**
- **Natural Dye**
- **Dye Extract**
- **Wet colour paste**
- **Herbal-Gulal with fragrance**
- **Herbal-Gulal dries**
- **Removal of solvents and drying in Tray dries**
- **Herbal-Gulal with fragrance**
- **Blending under specific conditions**
- **Dispersion in suitable solvent**
- **Extracted by usual procedures**
- **Natural ingredients in appropriate proportions**
- **Pulverization to fine powder**
- **Mixing with natural fragrance agent**

Manifold option of the procedure

The process provides a wide range of herbal dry colour compositions using different amounts of natural dyes with natural ingredients in different proportions. Different shades of various colours from light, medium or dark could be developed using different amount of dye(s) and mordants. More than 50 shades of herbal **gulals** have already been prepared at NBRI. There is a lot of creativity in using different types/concentrations of dye(s) and fixing agents. Hundreds of shades could be developed. Different natural fragrance viz. rose, sandalwood, jasmine, citronella etc. can also be used depending upon choice and colours of the herbal **gulals**.

**Main advantages of the process**

1. It provides an option to replace synthetic dye based dry colour composition by natural ones, which is safe, stain-free and eco-friendly. Presently, there are no options except to use synthetic based colours.
2. The powder provides a synergistic mixture of coloured dry powder, which has good sticking capacity to skin and can be easily removed by soft mop. The dry colours have cosmetic effect on skin too as they make face feel a bit soft.
3. The people who are scared of celebrating Holi because of the use of toxic synthetic dye based **gulals** which not only damage the skin but cause considerable pain to remove it but now have option to celebrate the festival.
4. The dry coloured powders can be used for cultural dances and making **rangoli** in houses.
5. The raw materials for natural ingredients of food, commercial or pharmaceutical grade are available in market.
6. The herbal gulals can be manufactured at higher scale or cottage level.

**IPR and Technology Transfer of the Process**

The complete specification of patent entitled *A process for the preparation of herbal dry colour composition for direct skin application and other purposes* has already been filed by Intellectual Property Management Division, CSIR on 18.7.2000 vide no. 244/DEL/2000 at Indian Patent Office, New Delhi.

In order to create awareness in public regarding the adverse effects of synthetic dyes and more usage of natural dye based products, 250 kg of herbal gulals of seven colours have been prepared at laboratory scale and put up for sale at NBRI. The gulals were highly appreciated by masses, print and electronic media. Based on the novelty and popularity of the gulals a private company namely M/S D.M. Herbal, a division of D. Manoharlal (Shellac) Pvt. Ltd., Sakti, Dist. Campa Janjir, Chattisgarh approached the Institute for its technology transfer. The process technology has been licensed to the said company on 13th September, 2001. The company has installed the necessary infrastructure as required for the preparation of herbal gulals and production of the product is in process. The product would be available in 100 g packing having cost of Rs. 20=00. The herbal gulals would be scented by natural fragrance agents like sandal wood oil, jasmine oil, lemon grass oil, winter grass oil etc.

**CONCLUSION**

The present invention relates to a process for the preparation of synergistic herbal dry colour composition by blending of natural dyes with natural ingredients in specific proportions and under specific conditions. The resultant colour powders thus prepared have synergistic action of natural dyes and natural ingredients resulting in good sticking capacity to skin and easily removable by soft mop. The production profile of dry colour composition is eco-friendly as no toxic effluents are released during preparation and application and do not disturb the ecological balance. The novel process yields herbal dry colour composition using natural dyes and natural ingredients thus providing an option / alternative to replace synthetic dye based dry powders by natural ones for direct skin application in Holi playing, traditional dances and other purposes.

**References**

10. Compendium of Inter-Regional Workshop on Natural Dyes, ed. Q.M. Humayun, National Handloom Development Corporation (NHD), Lucknow.