

PREPARATION OF EMULSIONS FROM FUNCTIONALIZED WASTE POLYETHENE WAXES AND THEIR APPLICATIONS ON WOOD AND LEATHER

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ABSTRACT

Pyrolysed waste polyethene waxes were functionalized under nitrogen condition by maleinisation process with maleic anhydride, and the product was then esterified with ethylene glycol and glycerol, in the absence of any catalyst. The melting points of the maleinated and esterified waxes were in the range of 48-78 °C. Viscosity measurements of the maleinated and esterified waxes showed decreased molecular weights of the waxes as the temperature and time of pyrolysis of the waxes increased. The esterified waxes were further compounded with toluene, oleic acid, morpholine and distilled water to produce the emulsions. The emulsions produced were applied on wood and leather, which adhered and dried. The coated substrates showed decrease in water absorption coefficients compared to the uncoated surfaces. Coated leather showed better marking-off properties than the wood coated substrates. The emulsions applied on wood finishing show good absorption properties which can be used as undercoat emulsion for wood.

Keywords: emulsions; esterification; maleinisation; marking-off properties; water absorption coefficients **Correspondence:** httk227@gmail.com, +2348032060944

INTRODUCTION

Polyethene (PE) is the most commonly used commodity plastic in the environment and one of the commonest wastes that are found across all communities in Nigeria. The increasing menace of waste PE littering the environment causes environmental pollution [1, 2]. Based on the report from the United Nations, the waste plastic dumps in the Nigerian environment increased by about 116% in 5 years to 1.25 million tonnes [3]. Polyethene products are non-biodegradable, and they constitute health and environmental hazards, encourage the spread of waterborne diseases, constitute a dirty environment, and can cause suffocation in small children and animals [4]. Control of environmental pollution by waste recycling is the best method of reducing bulk of the residue requiring disposal. Waste PE recycling is an act of treating waste PE materials like used water sachets and others waste PE in such a way they can be used again.

Polyethene as the most commonly used polyolefin has no polar functional groups in its backbone to provide reactive sites [4, 5]. Polyolefin modified by the introduction of polar groups in their backbones improves the physicochemical properties of the parent polymers and promotes adhesion, dyeability, cross-linking, or other chemical modifications [4, 6–9]. Maleinisation of polyethene is a process for preparing modified polyolefin waxes having improved hardness and gloss. It is usually done by reacting a waxy polyolefin (having a molecular weight of 400-5000) with maleic anhydride at a temperature of 120°C – 300°C under atmospheric or higher pressure in the presence or absence of a catalyst or a reaction initiator to produce a maleinised or maleinated polyolefin waxes [10].

According to Evrim [6], maleinisation of oils and fatty acids is of particular importance as a first step in the manufacture of water dispersible and watersoluble systems. It is also a useful method of introducing controlled chain branching into an alkyd resin. The reaction between maleic anhydride and conjugated fatty acids proceeds readily by Diels Alder type addition at moderate temperatures of about 120°C, according to Scheme 1.



Scheme 1: Maleinisation of conjugated fatty acid [6]

When non-conjugated fatty acids are involved, the reaction proceeds by attack on the active methylene groups and requires temperatures of about 200°C [6]. This type of reaction is more commonly encountered in resin manufacture other than the Diels Alder type and it takes place as follows:

Scheme 2: Maleinisation of unconjugated fatty acid [6]

The maleinised oils tend to be dark in colour, coatings based on them, have a tendency to be yellow due to the use of unsaturated drying oils [6]. Grafting and crosslinking of polyolefins in the melt are very important and are characterised by the formation of gels [11]. The Researchers further stated that grafting of polyolefins with maleic anhydride leads to an introduction of polar functionalities, which significantly improve its surface free energy and mainly polar fraction [11].



Scheme 3: Structure of maleic anhydride grafted polyethene [12].

Esterification is the chemical process for making esters; these are compounds of the chemical structure RCOOR', (R and R'are either alkyl or aryl groups). The most common method for preparing esters is to heat a carboxylic acid (R-CO-OH) with an alcohol (R'-OH) while removing the water that is formed. A mineral acid catalyst is usually needed to make the reaction occur at a faster rate [13]. The esterification reaction is both slow and reversible. The equation for the reaction between an acid (RCOOH) and an alcohol (R'OH) where R and R' can be the same or different is given [14] as Equation 1:

 $RCOOR' + H_2O$

Studies show grafted waxes are utilized for fuel production [15–26], practical applications like wax-graft copolymer compounds in carbon paper inks [10], monocyclic aromatics [27], and lubricants [28], though limited research has been conducted on emulsion preparation. This research work is justified in that it aims at minimizing the amount of waste PE in the environment by adding value to the waste for useful domestic purposes. Polyethene waxes modified with maleic anhydride and subsequently reacted with dihydric and polyhydric alcohols are found to be suitable for the preparation of emulsion [29].

An emulsion is a thin light-sensitive coating on a medium such as gelatin on film. It has been necessary from the view point of appearance and protection to repeatedly polish articles such as the floors of building made from tiles, plastics, etc., furniture, metals and plastics; the outer surface of car bodies; and the likes [29].

Many materials absorb moisture when immersed in water or when they are placed in a humid atmosphere [30]. The study mentioned that understanding water absorption by substrates during soaking is of practical importance, since it affects the mechanical properties of the product. He added that all strength properties decrease as substrates absorb moisture in the hygroscopic range. Khazaei also stated that one of the most important aspects of substrates ----- Equation 1 technology is modelling of the water absorption processes [30].

MATERIALS AND METHODS

Materials

The equipment used in the study include NDJ-8S digital rotary viscometer, Nicolet-IR100 FT-IR spectrophotometer, heating mantle, melting point apparatus, 2 - litre four-necked reactor, Hanna Hl 991000 pH meter, reflux condenser and Charles Austin suction pump. Waste Polyethene waxes pyrolysed at different temperatures and time reported elsewhere [31] were used; P200S1and P200S2 samples pyrolysed at 200°C for 1 hour and 2 hours without purging with nitrogen at the end of the reaction respectively. P200S3N and P250S1N samples pyrolysed at 200°C and 250°C for 3 hours and 1 hour purged with nitrogen at the end of the reaction respectively.

Preparation of maleinated wax

The pyrolysed wax 200 g; obtained above were placed in a 2-litre flask and 22 g of maleic anhydride was added. The mixture was heated to 240°C under reflux in nitrogen atmosphere. The temperature was then maintained under agitation for 4 hours. This was followed by distillation of the unreacted maleic anhydride from the system at a temperature of 150°C and reduced pressure for 30 minutes. The results gave brown-black coloured products. Product P200S2 was first reacted with 22 g of maleic anhydride at 100°C for 4 hours and it gave a hard, sticky but lighter coloured residue. This product was further taken back for second reaction after adding 2 g of maleic anhydride to top up the distilled one. This gave a light coloured residue.

Esterification of maleinated wax

Each of the products above 20 g, was introduced into a 2-litre round-bottom flask and then purged with nitrogen gas, followed by slow addition of 6% of ethylene glycol (on weight of the wax) over a period of 5 - 10 minutes at 140°C under agitation. The resulting mixture was further agitated for an additional 3 hours and thereafter distilled at 150°C at reduced pressure for 1 hour to remove the unreacted ethylene glycol therefrom. This procedure was repeated with glycerol.

Determination of saponification value

The maleinated wax 4 g (m) was placed into a round bottom flask fitted with a reflux condenser. 25 cm³ of alcoholic KOH was added and the mixture was heated under agitation for 30 minutes. It was then allowed to cool. The pH of the sample was continually measured with the addition of 2 cm³ of 0.5 M HCl at intervals. A blank test under the same condition but excluding the wax was also carried out. The end-point of the titration was determined from the curves of change in pH with volume of HCl. The same procedure was repeated with the esterified waxes. The saponification values were then calculated by Equation 2:

$$SV = \frac{28.05(n_2 - n_1)}{m}$$
 ------ Equation 2.

Where n_1 is the end-point for the wax, n_2 is the endpoint for the blank sample and m is the mass of the wax used. Results are shown in Figure 3.

Determination of Iodine Value

The maleinated wax 0.3 g (W), was dissolved in 10 cm³ of carbon tetrachloride and then treated with 20 cm³ of Wijs' reagent. The stopper of the flask was moistened with potassium iodide before being kept in the dark for 1 hour. The solution was then mixed with 15 cm³ of 10% KI, 100 cm³ of distilled water and titrated with standard sodium thiosulphate solution (0.1M). An average titre value "b" was obtained. A blank determination was also carried out in the absence of the maleinated wax and the average titre value "a" obtained. Hence, the iodine value was calculated using Equation 3.



The iodine values of the esterified waxes were also determined using the same procedure, and the results are shown in Figure 4.

Viscosity measurements

Dilute solution viscosity measurements of the maleinated and esterified waxes were carried out using Ostwald viscometer. Toluene was used as solvent and measurements were carried out with the viscometer placed in a constant temperature bath of 29°C. The limiting viscosity was computed according to known method, which is a plot of reduced viscosity against concentration [32]. The results are shown in Figure 5.

Emulsion preparation

The esterified waxes were compounded with other ingredients at room temperature to produce the emulsions. The following formulation was used for the preparation.

Table 1: Weight Percentage of Ingredients used inEmulsion Preparation

Materials	Weight (%)
Esterified wax	15
Toluene	20
Oleic acid	8
Morpholine	8
Water	49

The esterified waxes were dissolved in toluene and then oleic acid, morpholine and the distilled water were added respectively with continuous stirring.

Infrared spectroscopy

The Infrared spectroscopy analysis of the waxes and the emulsions was determined using KBr method on Nicolet-IR100 FTIR spectrophotometer. The technique is capable of detecting specific functional groups in polymers thereby helping in their identification and characterization [33].

Coating of substrates

The prepared emulsions were applied onto wood and leather using brush, as presented in Plate 2.

Water absorption test of substrates

The water absorption coefficients determination gives an idea of the water uptake of the coated substrates compared to the uncoated ones. The ability of the coated substrates to resist water uptake compared to the uncoated substrates can then be observe. Substrates were cut to approximate dimensions of $5 \times 2.5 \text{ cm}^2$. One face of the substrates was used for test. The other sides were coated with wax to stop water uptake through their sides. The initial moisture contents of substrates were obtained. Water absorption data were obtained by placing the substrates in 2-litre screw-cap flask containing distilled water. Tests were conducted at 25 \pm 0.5°C for immersion periods ranging from 30minutes to 24 hours. After soaking, the moisture content of substrates was calculated based on the increase in the substrate weight at corresponding times. At regular time intervals, ranging from 30 minutes at the beginning to 3 hours during the last stages of the process, the substrates were rapidly removed from the flask and superficially dried on a large filter paper to eliminate the surface water. The substrates were then weighed to determine the moisture uptake. The substrates were subsequently returned into water and the process was then repeated. Finally, curves showing the cumulative weight gain versus the square root of time were plotted, and linear regression curves were computed for each substrate. The water absorption coefficients of the substrates were determined by using Equation 4 (30):

$M_w = A\sqrt{t}$ ------Equation 4

Where, M_w is the amount of water absorbed in kg/m², and A is the water absorption coefficient (Kg/m².S^{1/2}). Following the definition, the water absorption coefficient, A is given by the slope of the fitted curve divided by the contact area. The water absorption coefficients for the coated substrates were then calculated and recorded; the results are shown in Figure

Marking-off test of coated substrates

This method is intended for assessing the resistance of the coated substrates to marking-off. A piece of filter paper 5cm x 5cm was placed on each of the coated substrates 5cm x 4cm so that an area of 5cm x 1cm of the filter paper was not in contact with the coated substrates. The substrates were covered with a glass plate 5cm x 5cm and a weight of 1 Kilogram was placed on the glass plate. The substrates were kept in the oven at 60°C for 4 hours. This is B.S. 3662/5 marking-off test standard. The staining of the filter papers was assessed with the standard Grey Scale for assessing stain as marking-off of the coated substrates. The assessment was observed and recorded as shown in Figure 8.

RESULTS AND DISCUSSION

Maleinisation of pyrolysed waxes

Generally, the maleinisation of the pyrolysed wax gave brown-black waxy residues (Figure 1). Products P200S1 gave soft waxy residue. Product P200S2 gave a light brown-black coloured and less-waxy residue after further maleinisation with 2 g of the maleic anhydride (to make up for the distilled maleic anhydride during the first maleinisation process). Products P200S3N and P250S1N gave softer residues compared to products P200S1 and P200S2 are shown in Figure 1.



Figure 1: Maleinated waxes

The maleinisation of the pyrolysed waxes gave brown-black products. This is an indication of the reaction of maleic anhydride and the pyrolysed waxes. Evrim [6], in his research illustrated that maleinised oil tends to be dark in colour. The proposed reaction for the maleinisation of the pyrolysed wax and maleic anhydride is as follows:





Scheme 4: Reaction of pyrolysed unconjugated wax with maleic anhydride

It is also possible for the pyrolysed wax to have two double bonds, which can be conjugated or unconjugated [6]. The conjugated chain is proposed to react with the maleic anhydride as shown in Scheme 5:



It is possible for the maleic anhydride to retain its unsaturation as shown in scheme 7. Shi *et al.* [34] in their research, proposed a mechanism formed by melt reactive grafting of polypropylene with maleic anhydride in which the maleic anhydride maintained its double bond.



Scheme 7: Reaction of pyrolysed wax with maleic anhydride involving substitution of hydrogen

This is also applicable to the conjugated or unconjugated bonds of the pyrolysed wax as earlier proposed in schemes 4 and 5.

Esterification of maleinated waxes

The esterification of the maleinated waxes gave same brown-black residues (Figure 2) but softer than the maleinated waxes before esterification. The maleinated waxes as acid-modified waxes reacted with ethylene glycol and glycerol.

and the			States
P200S1EE	P200S2EE	P200S3NEE	P250S1NEE
			A B
P200S1EG	P200S2EG	P200S3NEG	P250S1NEG

Figure 2: Esterified waxes

The esterification reaction between the maleinated wax and the alcohols are proposed as follows: 1. Reaction with ethylene glycol



Scheme 12: Esterification of maleinated wax with two molar equivalents of glycerol

Reference to scheme 7, the reaction is proposed to be:



Scheme 13: Esterification of maleinated wax with glycerol with unsaturation on the maleic anhydride moity.

Melting temperatures of waxes

The results of the melting temperatures of the maleinated waxes and the esterified waxes were shown in Table 2. The average melting temperatures for the maleinated products P200S1, P200S2, P200S3N and P250S1N are 63°C, 72°C, 50°C and 57°C respectively. Product P200S3N which was pyrolysed at 200°C for 3 hours showed a drop to an average of 50°C. This showed

decrease in melting temperature of the wax as the time of pyrolysis increase. Product P200S2 has the highest melting temperature which might be due to the excess maleic anhydride that reacted during the second reaction. The results showed that products with lower melting temperatures were likely to have lower molecular weights.

Table 2: Melting Temperatures of the Waxes

	Maleinated wax (°C)	Esterified with ethylene glycol (°C)	Esterified with glycerol (°C)
P200S1	61-65	58-63	58-65
P200S2	61-65	71-77	72-78
P200S3N	48-52	49-52	50-52
P250S1N	55-59	52-56	53-58

The results in Table 1 showed little or no difference between the melting temperatures of the waxes esterified with either ethylene glycol or glycerol with that of their counterpart maleinated waxes.

Saponification values of waxes

The saponification values of the maleinated and esterified waxes were calculated using the peaks in the plots of change in pH with change in volume of HCl used as the end-point of the titration. The results are shown in Figure 3. The saponification values for the maleinated products P200S3N and P250S1N are higher than the values of the other products. This shows that products P200S3N and P250S1N have lower molecular weights than the other products. Gopinant *et al.*, [35] in their research indicated that saponification value decreases with increasing weight percentage of unsaturated fatty acid esters. This corroborated with the percentage yields and viscosities of the waxes reported elsewhere by Umaru *et al.* [31] and melting temperatures in Table 2.



Figure 3: Saponification values of waxes

The saponification values of the esterified waxes rather gave conflicting results. Whereas the values for P200S1 and P200S2 are higher than their maleinated counterparts, those of P200S3N and P250S1N gave much lower values. The reason for this discrepancy can be explained from the iodine values of the waxes given in Figure 4.

Iodine values of waxes

The calculated iodine values of the maleinated and esterified waxes are shown in Figure 4. The iodine values of the waxes are indication of the degree of unsaturation of the samples.



Figure 4: Iodine values of waxes

The iodine values of the waxes are within a range of 34 – 53 which seemed to increase with time and temperature. The maleinated wax pyrolysed at 250°C for one hour gave the highest iodine value. The iodine values given in Figure 4 of waxes esterified with glycerol indicate that P200S1, P200S2 have much lower iodine values than that of P200S3N and P250S1N. This indicated that the latter are more unsaturated than the former. However, the presence of more than one double bond in a chain can result into two scenarios, which could be conjugated or unconjugated [6]. In the case of conjugated double bonds, only one maleic anhydride could be taken by a chain as indicated by Evrim in Scheme 1. According to Blicq, [36] the iodine value

obtained for samples containing conjugated double bonds is empirical since the reagent does not react stoichiometrically with conjugated unsaturation. For unconjugated samples; the iodine value obtained is a measure of the total unsaturation [35]. The unsaturation originated from the degradation of the waxes that had taken place during pyrolysis irrespective of maleinisation or esterification. Gopinant *et al.* [35] in their research showed that iodine value increases in weight percentage of unsaturated fatty acid esters. It is possible for iodine value of the waxes to increase as a result of the maleic anhydride retaining its unsaturation after maleinisation [35]. The development of the unsaturation was shown in the infrared spectra of the waxes, where it presented C=C stretch and C-H bend (alkene).

Viscosity measurement

The viscosities of the maleinated and esterified waxes were deduced from the plots of reduced viscosity with concentration, and the given intrinsic viscosities observed serves as an indication of the molecular weights of the waxes. The intrinsic viscosities obtained for the different waxes are shown in Figure 5. The intrinsic viscosity of the maleinated waxes decreased with increase in time of pyrolysis which shows decrease in molecular weight with increase in time of pyrolysis. There is also a drop in intrinsic viscosity of the wax pyrolysed at 250°C compared to P200S1 pyrolysed at lower temperature; 200 °C. P200S2 has lower intrinsic viscosity which might be due to the further reaction that had taken place with the added 2 g maleic anhydride. This is clearly shown in the results of saponification values and melting points of the waxes in Figure 3 and Table 2 respectively.



Figure 5.Intrinsic viscosity of waxes

Figure 5 showed decrease in intrinsic viscosity of the esterified waxes compared to its corresponding maleinated waxes. The waxes esterified with glycerol have higher intrinsic viscosity values than the waxes esterified with ethylene glycol. This might be as a result of the glycerol having higher molecular weights than ethylene glycol. This is so due to higher molecular weight of glycerol being a trihydric alcohol than the ethylene glycol being dihydric alcohol.

Infrared spectra

The functional groups of the waxes were identified from their infrared spectra. The infrared spectra are used to identify the functional groups in a compound. The pyrolysed waxes showed C-H aliphatic stretch, C-H aliphatic bend, C-C stretch and C-H bend (alkene) and bands for C=C stretch (Figure 6a). Bands above 1518 cm⁻¹also observed which confirmed the presence of C=C stretch (alkene). This indicates some degree of unsaturation of the waxes before maleinisation. Maleinated waxes showed C-O stretch at around 1460 cm⁻¹ band. Bands around 1710-1715 cm⁻¹observed indicating C=O stretch (acids). Bands of C-O stretch and C=O stretch observed in the spectrum (Figure 6b) of the maleinated waxes justified maleinisation reaction had taken place between maleic anhydride and the pyrolysed waxes. Esterified waxes indicate bands for C-H stretch (aliphatic), C=O stretch (acids), C-H bend (aliphatic) and C-H bend (alkene). Combination of O-H stretch and C-O stretch around 2290 cm⁻¹, O-H stretch (H-bonded) first overtones around 1600 cm⁻¹ and O-H bend around 1373 cm⁻¹ were also observed. The presence of O-H bands indicates the evidence of esterification reaction between the functionalized waste polyethene waxes and the alcohols [13].

In addition to the bands observed in spectra of the esterified waxes, the spectra of the emulsions (Figure 6d) showed O-H stretch (free) above 3600 cm^{-1} , N-H stretch primary amine above 3400 cm^{-1} , O-H bend at 2091 cm⁻¹, N-H bend (amine) around 1650 cm^{-1} , C=C stretch (aromatic ring) around 1552 cm^{-1} , C-N stretch (amine) around 1313 cm^{-1} and =C-H (out of plane bending) and ring puckering or may be due to N-H wagging on H-bonding at 869 cm^{-1} - 880 cm^{-1} .

Combination bands are also observed for O-H stretch plus O-H bends around 2507 cm⁻¹ and O-H stretch plus C-O stretch above 2100 cm⁻¹. The appearance of bands for N-H stretch, N-H bends and C-N stretch (amines) is evidence of the reaction of the esterified waxes and morpholine. Bands of C=C stretch (aromatic rings) around 1552 cm⁻¹ indicates presence of toluene.

Presence of more O-H stretch (free) and combinations bands for O-H stretch plus O-H bends indicates presence of oleic acid and water used in emulsions preparation.



Figure 6: Spectra of waxes and emulsion

Prepared Emulsions

The prepared emulsions are shown in Plate 1.

P200S1EE Emulsion	P200S2EE Emulsion	P200S3NEE Emulsion	P250S1NEE Emulsion
	(all all all all all all all all all all	1000	
P200S1EG Emulsion	P200S2EG Emulsion	P200S3NEG Emulsion	P250S1NEG Emulsion

Plate 1: Prepared emulsions

Coating of Substrates

The emulsions (Plate 1) applied on wood and leather substrates respectively were dried as shown in Plates 2.



Plate 2: Uncoated and Coated Wood and Leather respectively

Water absorption of coated substrates

The water absorption of the uncoated and coated substrates was calculated using the slopes on plots of Cumulative water gain with $t^{1/2}$ of wood and leather coated with the emulsions. The calculated water absorption coefficients A, of the coated and the uncoated substrates were recorded as shown in Figure 7.



Figure 7. Water absorption coefficients of substrates

Figure 7 showed decrease in water absorption coefficient of the coated substrates compared to the uncoated substrates. Understanding water absorption by substrates during soaking is of practical importance, since it affects the mechanical properties of the product [30]. Moisture can decrease the strength properties of the substrates with increase in water/moisture absorption when exposed to the environment during usage. Micro-organisms might also act on the moist substrate, thereby damaging it.

The decrease in water absorption coefficient of the coated substrates over uncoated suggests increased strength properties. All strength properties decrease as substrate adsorbs moisture in the hygroscopic range [30]. This means that the emulsion prepared can be used on wood and leather since it reduced its water absorption.

Marking-off of Coated Substrates

Figure 8 showed the marking-off assessment of the coated substrates observed. The marking-off assessment of wood substrates coated with P200S1EG, P200S1EE, P250S1NEE, P250S1NEG, and P200S3NEG are relatively poor having an assessment of 2, 2/3 and 3 respectively. Whereas P200S3NEE, P200S2EG and P200S2EE gave relatively fair results with stain assessment of 3/4 and 4 respectively, which are good. The assessment of the marking-off of leather coated substrates is 4/5 to 5 which shows a very good markingoff assessment. This shows that the emulsions have a better marking-off on leather compared to wood. This suggests that the emulsions prepared are suitable on leather as polishing emulsions. According to Vipond [37], regardless of the purpose of the substrate, maintenance may involve ensuring that the substrate is preserved as intended.



Figure 8: Marking-off assessment of coated substrates

CONCLUSION

The melting points of the maleinated and esterified waxes are in the range of 48-78°C. The saponification values for the maleinated products P200S3N and P250S1N are higher than the values of the other products, these shows to have lower molecular weights than others. The iodine values of the waxes are within a range of 34-53 which seem to increase with time and temperature. Viscosity measurements of the maleinated and esterified waxes also showed a decrease in molecular weight of the waxes as the temperature and time of pyrolysis increased. The FT-IR spectra of the maleinated waxes presented anhydride bands at around 1710-1715cm⁻¹ and the esterified waxes have additional bands for O-H bonds.

The esterified waxes were then compounded into emulsions. The emulsions produced were applied on wood and leather to which they adhered and dried. The coated substrates showed decrease in water absorption coefficients compared to the uncoated ones. The coated leather showed better marking-off assessment compared to the coated wood finishing.

The emulsions prepared can be used as undercoat in wood finishing which will effectively reduce the amount of water absorption by the wood. They can also be used on leather as polishing emulsion, having good marking-off properties. Thus, the production of emulsion from modified waste PE waxes reduces environmental pollution and recovers valuable by-products (emulsions). It also serves as a means of creating job opportunities for the people.

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