Full Length Research Paper

Preparation of Overbased Liquid Micro Emulsion Stabilizers for Halogen Containing Polymers

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Poly (vinyl chloride) (PVC) is one of the most important commercial plastic materials, but it is thermally unstable at processing temperature. Processing of PVC at elevated temperatures requires the use of thermal stabilizers. This research work report the preparation, characterization and evaluation of metal carboxylates from fixed oils [locally available vegetable oils] that can function as PVC and or, other halogen containing polymers thermal stabilizers. A liquid micro emulsion stabilizer composition for stabilizing halogen-containing polymer consist of a micro emulsion of an overbased metal carbonate/carboxylate obtained from the reaction of an oxide and/or hydroxide of a metal selected from the group consisting of sodium, potassium, calcium, magnesium, zinc and mixtures thereof, an aliphatic carboxylic acid in which the aliphatic moiety contains up to about 30 carbon atoms and carbon dioxide in the presence of a solvent for the aliphatic carboxylic acid, a promoter and a micro emulsion-forming amount of surfactant. Overbased micro emulsion stabilizers were prepared from four commercially available vegetable oils (Ground nut oil, Coconut oil, Soya oil and Palm Kernel oil).These oils were hydrolysed and the physico-chemical properties of the oils before and after hydrolyses were examined. Their micro emulsions were digested to determine the amount of metal concentration using Atomic Absorption Spectrophotometer (AAS).

Keywords: Overbased liquid micro emulsions, stabilizers, and halogen containing polymers.

INTRODUCTION

PVC is almost certainly the least naturally stable polymer in commercial use. During processing, storage and utilization, PVC degrades as it is exposed to high temperatures, high mechanical stresses or ultraviolet light, all in the presence of oxygen. Degradation of the polymer occurs by successive elimination of hydrogen chloride (HCl), which is called dehydrochlorination, yielding long polyenes (primary reaction), Scheme 1, which is consequently causing discoloration, deterioration of the mechanical properties and a lowering of the chemical resistance. Subsequent reactions of highly reactive conjugated polyenes crosslink or cleave the polymer chain, and form benzene and condensed and/or alkylated benzenes in trace amounts depending on temperature and available oxygen (secondary reactions), scheme 2.

The degradation of PVC at elevated temperatures required in thermoplastic processing is an intrinsic characteristic of the polymer and consists of dehydrochlorination, auto-oxidation, mechano-chemical chain scission, crosslinking, and condensation reactions. This degradation must be controlled by the addition of stabilizers. The heat stabilizer must prevent the dehydrochlorination reaction that is the primary process in degradation. There are two ways the stabilizer can act: By reacting with allylic chlorides, the intermediates in the zipper degradation chain. This process should be faster than the chain propagation itself, requiring a very active nucleophile. However, the reactivity of the nucleophile should not be so high as to react with the secondary chlorine of the PVC chain, a process that rapidly exhausts the stabilizer. To be effective, the stabilizer must be associated by complex formation with polymer chlorine atoms, which means it should have a
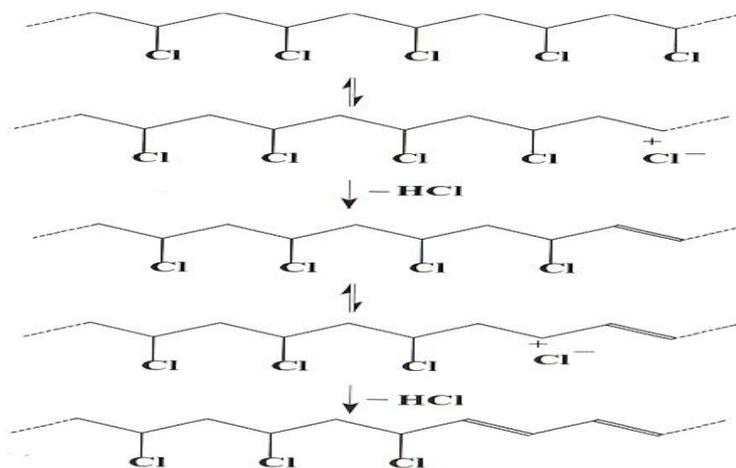
Scheme 1
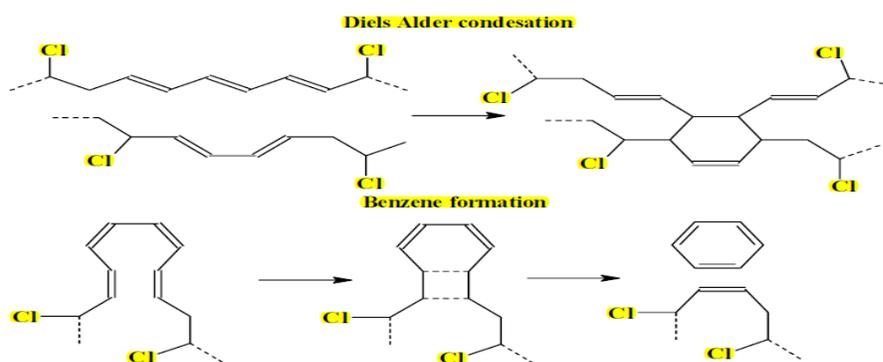
Scheme 2

Lewis acid character. This association should take place in regions where the polymer molecules have maximum mobility; in other words, where the conformation of the polymer can favor the degradation processes. Once the degradation starts, it is very fast and can be stopped only if the stabilizer is already associated with the chlorine atom that becomes allylic. These regions are the surfaces of the primary particles of PVC, where the stabilizer molecules are associated with the chlorine atoms. The exceptional effectiveness of such stabilizers at very low concentrations is explained by their entropically favorable position for stopping degradation. In general, these stabilizers, because of their effectiveness, prevent the formation of polyenes longer than four to five double bonds and maintain very good early color in the polymer. These stabilizers are called primary stabilizers. Scavenging the hydrogen chloride generated by degradation is another way to stop the process as the HCl is a catalyst for the chain propagation reaction and the initiation step. However, the diffusion of HCl is quite slow because HCl is associated with the double bond where it was generated. When HCl diffuses away from the reaction centre, the zipper degradation reaction stops. The stabilizer should scavenge HCl with high effectiveness to avoid its catalytic effect in chain initiation that starts another zipper dehydrochlorination chain. Because this type of stabilizer cannot prevent the dehydrochlorination in its early stages, polyenes longer than four to five double bonds are formed. PVC discolors and the initial color is not maintained. However, by scavenging HCl, this type of stabilizer avoids the autocatalytic degradation and consequently, overall degradation is much slower. These stabilizers provide very good long term stability and are usually referred to secondary stabilizers. To have good stabilization of PVC with good early color and long term stability, the two types of stabilizer should be combined appropriately for each particular PVC formulation.

Stabilization is complicated by the fact that primary stabilizers become strong Lewis acids by reacting with the HCl that catalyzes the initiation and propagation of PVC degradation. To avoid this, secondary stabilizers should react efficiently with HCl to protect the primary stabilizers. Another possibility is to include compounds called costabilizers in the system. Co-stabilizers form relatively stable complexes with the chloro derivatives of primary stabilizers (the Lewis acids) and suppress their degradative effect.

The main classes of thermal stabilizers in current use are lead salts, metal soaps and organo-tin compounds. Some of these have disadvantages in terms of toxicity, environmental pollution and/or high cost (Lin et al., 2006). The metal soaps and organo-tin stabilizers are safer than lead salts, but their stabilization effects are usually lower than those of lead salts. In fact, calcium and zinc soaps of some seed oils had been investigated and proved to be save thermal stabilizers of PVC (Folarin and Sadiku, 2011). As a result of the worldwide increase in environmental awareness, attention is currently being focused on thermal stabilizers that are non-toxic and environmentally friendly (Bao et al., 2008). Thermal stabilizers of PVC possess one or more of the following features in addition to capacity for absorption and neutralization of HCl evolved by PVC during degradation:
1. An ability to replace or displace active, labile substituent groups, such as tertiary and allylic chlorine atoms
2. A capacity to render pro-degradant substances e.g. heavy metal chlorides, inactive and
3. An ability to modify chain reactions, by interrupting conjugated polyene formation and inhibiting the elimination of HCl.

An ideal stabilizer should possess a number of desirable secondary attributes. Such stabilizers should be colourless, compatible and non-migrating. It should be relatively inexpensive, non-toxic, odourless and tasteless, and should not affect the polymer's physical and rheological characteristics.

Experimental

The vegetable oils were bought in their pure form from the surrounding area of the Federal University of Technology Akure, Ondo State, Nigeria. The oils were hydrolysed by refluxing 10g of each sample with 150ml of 0.5N ethanolic potassium hydroxide for one hour. Distilled water H_2O (150ml) was added and acidified with dilute hydrochloric acid (about 60ml) followed by addition of 150ml of hexane [3]. The hexane layer was removed using a separatory funnel. The sample oils and the hydrolyzed fatty acids obtained were characterized. All chemical used for this experiment are of analytical grade

(sigmoid and Merck) and the weighing balance used was mettler balance model AE 160. Into a 3-L resins flask, was charged paraffinic oil (176.2 g), oleic acid obtained from the hydrolyzed oil samples (216.6 g), ZnO (31.2 g) and 20 ml of water. The mixture was heated to 104^0 C. with vigorous agitation until the contents became clear. The reaction temperature was increased to 140^0 C. and 15 ml water was removed. An additional 31.2 g of ZnO was added to the flask and agitation was continued for 5 minutes. 15 grams of sorbitol was then added and the reaction temperature was increased to 180^0 C. 20 grams of glycerin was charged and after a few minutes of agitation, carbonation was started at the rate of 240 ml/min of CO_2 for 5 hours. The reaction product was then filtered off solid materials. A brown product having 9.42 weight % zinc (5 weight % Zn as oleate and 4.42 weight % Zn as zinc carbonate) and a viscosity at 25^0C of 1165 cP was obtained (Fakinlede et al., 2003).

Digestion Procedure

About 0.5 g sample was weighed into dry, clean PTFE digestion vessel. One milliliter of double distilled water (DDW) was added first and then supplied with appropriate digestion mixture: HNO_3/H_2SO_4, 2 + 1 (v/v) for wet digestion. When the initial reaction has subsided, vessel contents were gently mixed and heated, first at low temperature (about 125 ∘C), then the temperature was gradually increased until heavy evolution of fumes ceases. The mixture was then heated again until complete digestion. The final residue (sulfuric acid and inorganic constituent) was dissolved in 2.5 ml of HCl and diluted to 50 ml with DDW. The same digestion procedures were carried out for blank solution, AOAC: Association of Analytical Communities, 1990

Atomic absorption analysis of samples

The digested microemulsion samples were analyzed for zinc metals concentration using Atomic Absorption Spectrophotometer, A Analyst 400, S/N 201S10114102 Auto sampler Model (Chem. Tech. Analytical) at the Central Science Laboratory Obafemi Awolowo University, Ile-Ife, Nigeria.

Physicochemical properties

Moisture content

The moisture content was obtained by using a known weight of the oil sample put into a clean previously weighted beaker and dried in an oven at 105^0C for 4 hours. The sample was taken from the oven, cooled in a

Table 1. Physicochemical characteristics of the four vegetable oils

Properties	Soya oil	palm kernel oil	groundnut oil	coconut oil
Refractive index	1.472	1.457	1.467	1.462
Specific gravity	0.941	0.903	0.908	0.907
Viscosity (cp)	253.28	111.74	433.67	403.39
Iodine value (meq/ kg oil)	4.6145	5.1914	9.2290	6.9218
Saponification value (mg KOH/ g oil)	16.27	33.09	39.83	31.97
Acid value (mg KOH/ g oil)	0.300	0.630	0.360	0.180
Free fatty acid (% as oleic acid)	15.00	31.50	18.00	9.00
Peroxide value (meq peroxide/ kg oil)	10.00 / 2.835	05.00 / 1.705	40.00 / 0.95	15.00 / 2.705
% Moisture contents	2.81	1.69	0.99	2.70

*Viscosity for palm kernel oil was carried out on a water bath at 60 ^{o}C

Table 2. Physicochemical characteristics of fatty acids of the four vegetable oils

Properties	Soya f.a	Palm kernel f.a	Groundnut f.a	Coconut f.a
Refractive index	1.351	1.354	1.349	1.359
Specific gravity	0.962	0.959	0.963	0.961
Viscosity (cp)	18.03	22.37	17.78	24.96
Iodine value (meq/ kg oil)	3.7013	1.5863	2.115	0.5288
Saponification value (mg KOH/ g oil)	0.45	0.22	0.11	0.34
Acid value (mg KOH/ g oil)	****	0.32	****	****
Free fatty acid (% as oleic acid)	****	2.820	****	****
Peroxide value (meq peroxide/ kg oil)	30.00	15.00	25.00	5.00
% Moisture contents	92.88	93.10	96.92	96.67

f.a- fatty acid, **** Undetermined

desiccator for about 30 minutes and then weighed. The procedure was repeated until a constant weight was obtained. The percentage moisture in the oil was then calculated.

Moisture, % = $\frac{\text{Original weight – Final weight}}{\text{Original weight}}$ x 100

And Dry matter, % = 100 – moisture, %

The refractive index was determined with calibrated Abbey refractometer using methods described by Dawodu and Omole (2000). The specific gravity of the sample oil was measured using specific gravity bottle and following the procedures described by Pearson 1976 [8] both refractive index and specific gravity were determined at ambient temperature of 25 + 0.5 ^{o}C. The acid, free fatty acid and perioxide values were determined and calculated according to the recommendation of AOAC (2000). While the saponification and iodine values were determined by standard method of AOAC (Association of Analytical Communities, 2000).

RESULT AND DISCUSSION

Calculations

Equation of Reaction:

2 CH_3 {CH_2}$_7$CH=CH {CH_2}$_7$COOH +2ZnO + CO_2 → [CH_3 {CH_2}$_7$COO$^-$]$_2$ Zn + $ZnCO_3$ + H_2O.
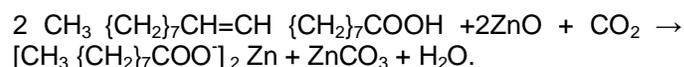
Mole ratio of Oleic Acid to Zinc Oxide = 1:1, Molar Mass of Oleic Acid = 282g^{-1}mole. Amount in mole of Oleic acid = 216.6g/282g^{-1}mole = 0.768 mole

Mole of Zinc Oleate = 0.768/2 = 0.384 mole, Mass of

Table 3. Concentration of Zinc (Zn) in mg/l of the microemulsion

Sample	Colour	Zn (mg/l)	Viscosity at 25°C (cP)
SY	Golden yellow	36.00	144.3431
PK	Brown	28.70	194.2944
GN	Deep Brown	79.40	221.0303
CN	Yellow	34.30	168.0407

Blank (mg/l): 0.00, Dilution factor (df) = 50/0.5 = 100

Table 4 % Concentration of Zinc (Zn) in the microemulsion

Sample	% Zn in the microemulsion	% Zn as Oleate	% Zn as Carbonate
SY	7.20	5.68	1.52
PK	5.74	5.68	0.06
GN	15.88	5.68	10.20
CN	6.86	5.68	1.18

Result: CSL STD 8

Zn 213.86
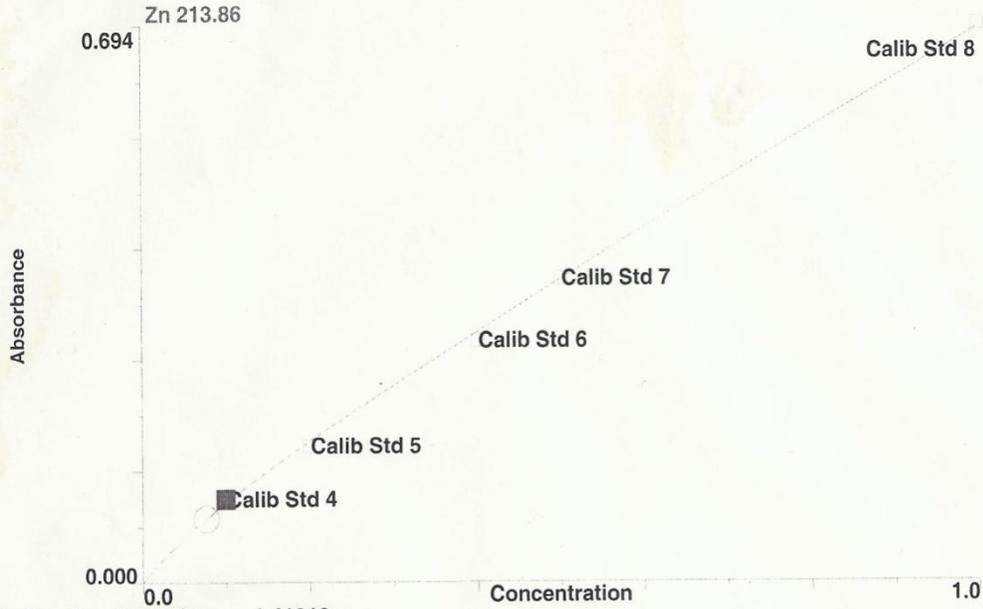
Calibration Curve Slope: 1.41912
Calibration Curve Intercept: 0.00000
Calibration Curve Correlation Coefficient: 0.999581
Calibration Curve Type: Nonlinear Through Zero
Current Sample Concentration: 0.077 mg/L

Std #	Standard ID	Entered Conc.	Calculated Conc.	Action
Blank	Blank	0	0.000	Include
1	Calib Std 1	0.01	0.079	Ignore
2	Calib Std 2	0.02	0.121	Ignore
3	Calib Std 3	0.04	0.139	Ignore
4	Calib Std 4	0.1	0.106	Include
5	Calib Std 5	0.2	0.193	Include
6	Calib Std 6	0.4	0.384	Include
7	Calib Std 7	0.5	0.502	Include
8	Calib Std 8	1.0	1.009	Include

8/24/2012 4:32:00 PM

```
=====================================================================================
Analysis Begun

Logged In Analyst: AAnalyst 200                    Technique: AA Flame
Spectrometer Model: AAnalyst 400, S/N 201S10114102Autosampler Model:

Sample Information File: C:\data-AA\AAnalyst 200\Sample Information\Isola Zn.sif
Batch ID:
Results Data Set: Isola Oladotun
Results Library: C:\data-AA\AAnalyst 200\Results\Results.mdb

=====================================================================================
Sequence No.: 36                              Autosampler Location:
Sample ID: Blank                              Date Collected: 9/27/2012 4:47:24 PM
Analyst:                                      Data Type: Original

-------------------------------------------------------------------------------------
Replicate Data: Blank
Repl   SampleConc   StndConc   BlnkCorr   Time        Signal
 #     mg/L         mg/L       Signal                 Stored
 1                  [0.00]     0.100      16:47:26     Yes
 2                  [0.00]     0.098      16:47:30     Yes
 3                  [0.00]     0.104      16:47:34     Yes
Mean:              [0.00]     0.101
SD:                0.00       0.0028
%RSD:              0.00       2.77
Auto-zero performed.

=====================================================================================
Sequence No.: 37                              Autosampler Location:
Sample ID: Sample GN                          Date Collected: 9/27/2012 4:48:03 PM
Analyst:                                      Data Type: Original

-------------------------------------------------------------------------------------
Replicate Data: Sample GN
Repl   SampleConc   StndConc   BlnkCorr   Time        Signal
 #     mg/L         mg/L       Signal                 Stored
 1     0.796        0.796      0.563      16:48:05     Yes
 2     0.792        0.792      0.560      16:48:09     Yes
 3     0.794        0.794      0.561      16:48:14     Yes
Mean:  0.794 X100   0.794      0.561
SD:    0.002        0.002      0.0013
%RSD:  0.274        0.274      0.24
```

79.4 mg/L

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=====================================================================================
Sequence No.: 38                              Autosampler Location:
Sample ID: Sample CN                          Date Collected: 9/27/2012 4:48:50 PM
Analyst:                                      Data Type: Original

-------------------------------------------------------------------------------------
Replicate Data: Sample CN
Repl   SampleConc   StndConc   BlnkCorr   Time        Signal
 #     mg/L         mg/L       Signal                 Stored
 1     0.345        0.345      0.275      16:48:52     Yes
 2     0.340        0.340      0.272      16:48:56     Yes
 3     0.345        0.345      0.275      16:49:01     Yes
Mean:  0.343        0.343      0.274
SD:    0.003        0.003      0.0018
%RSD:  0.792        0.792      0.66
```

= 343 mg/L

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=====================================================================================
Sequence No.: 39                              Autosampler Location:
Sample ID: Sample SY                          Date Collected: 9/27/2012 4:49:33 PM
Analyst:                                      Data Type: Original

-------------------------------------------------------------------------------------
Replicate Data: Sample SY
Repl   SampleConc   StndConc   BlnkCorr   Time        Signal
```

j

#	mg/L	mg/L	Signal		Stored
1	0.360	0.360	0.285	16:49:35	Yes
2	0.357	0.357	0.283	16:49:39	Yes
3	0.364	0.364	0.287	16:49:44	Yes
Mean:	0.360	0.360	0.285		
SD:	0.003	0.003	0.0021		
%RSD:	0.871	0.871	0.73		

≈ 36·0 mg/L

==

Sequence No.: 40   Autosampler Location:
Sample ID: Sample PK   Date Collected: 9/27/2012 4:50:11 PM
Analyst: Data Type: Original

Replicate Data: Sample PK

Repl #	SampleConc mg/L	StndConc mg/L	BlnkCorr Signal	Time	Signal Stored
1	0.285	0.285	0.235	16:50:12	Yes
2	0.286	0.286	0.235	16:50:17	Yes
3	0.290	0.290	0.238	16:50:21	Yes
Mean:	0.287	0.287	0.236		
SD:	0.002	0.002	0.0017		
%RSD:	0.868	0.868	0.72		

≈ 28·7 mg/L

Calibration data for Zn 213.86   Equation: Nonlinear Through Zero

| | Mean Signal | Entered Conc. | Calculated Conc. | Standard | |
ID	(Abs)	mg/L	mg/L	Deviation	%RSD
Blank	0.0000	0	0.000	0.00	2.8
Calib Std 4	0.1037	0.1	0.106	----	----
Calib Std 5	0.1699	0.2	0.193	----	----
Calib Std 6	0.3013	0.4	0.384	----	----
Calib Std 7	0.3778	0.5	0.502	----	----
Calib Std 8	0.6936	1.0	1.009	----	----

Correlation Coef.: 0.999581   Slope: 1.41912   Intercept: 0.00000

$ZnCO_3 = 90 \times 0.384 = 34.58g$ {RMM of $ZnCO_3 = 90$}. Mass of Zinc in Zinc Oleate = (62.4 - 34.58) g = 27.82g . % of Zinc as Oleate in the reaction vessel = $(27.82/490.2) \times 100 = 5.68$ %

From Table 1, Coconut oil has the lowest acid value (0.18 mg KOH/g of oil) and free fatty acid (9.00 % as Oleic Acid) among the four vegetable oils and Palm kernel oil has the highest Acid value (0.63 mg KOH/g of oil) and free fatty acid (31.50 % as Oleic Acid). Coconut oil has a very low unsaturated fatty acid. The Groundnut oil had high iodine values (9.229 meq/kg oil) and perioxide value (40 meq perioxide/kg of oil, thus reflecting a high degree of unsaturation and primary oxidation respectively. The values obtained for the physicochemical properties of the four vegetable oils after hydrolysis decreases except for the moisture content that increases significantly due to the removal of glycerol formed as part of the product of hydrolysis. However, comparing the physicochemical properties of the hydrolysed oil in Table 2, the fatty acid of the Soya oil has the highest iodine value (3.7013 meq/kg of fatty acid) and saponification value (0.45 mg KOH/g fatty acid) and perioxide value (30 meq perioxide/kg of fatty acid). Only Palm kernel oil shows a positive result for free fatty acid after hydrolysis (2.820 % as Oleic). Micro emulsion from palm kernel oil has the lowest % of Zn as Zinc Carbornate (0.27%) which shows that the higher the amount of Oleic Acid in the sample the less the amount of Zinc carbonate that will be formed. After digestion, a product having 15.88 weight % zinc (5.68 weight % Zn as oleate and 10.20 weight % Zn as zinc carbonate), 7.2 weight % zinc (5.68 weight % Zn as oleate and 1.52 weight % Zn as zinc carbonate), 6.86 weight % zinc (5.68 weight % Zn as oleate and 1.18 weight % Zn as zinc carbonate), 5.74 weight % zinc (5.68 weight % Zn as oleate and 0.06 weight % Zn as

zinc carbonate) were obtained for ground nut oil, soya oil, coconut oil and palm kernel oil respectively

CONCLUSSION

The physico-chemical properties of four commercial vegetable oils have been studied for their industrial application. The colour of their micro emulsions varies from yellow to dark brown. Three of the oils are liquids at room temperatures and one (Palm kernel oil) is semi-solid. Ground nut oil has the highest % of zinc after carbonation, followed by Soya oil and Coconut oil. The results obtained from this study could be used as baseline data to develop a good micro emulsion stabilizers from the oils examined for

the formulation of heat and chemical resistant halogen containing polymers (e.g PVC).

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