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THE SYNTHESIS OF OLEOCHEMICALS WITH MULTI-FUNCTIONAL GROUPS, THE OLEOCHEMICALS AND THEIR USES

FIELD OF THE INVENTION

The present invention relates to the synthesis of oleochemicals with multi-functional groups, the oleochemicals and their uses.

BACKGROUND OF THE INVENTION

In recent years, the global output of synthetic resins has been over 130 million metric tons. China has produced 10 MMT of synthetic resins, an increment of 18%. The development of plastics industry has drastically increased the demands for inorganic salts such as synthetic resins wherein the inorganic salts are used as fillers in the process of manufacturing the plastics.

It is reported that in 1990's, the growth rate of inorganic salts consumed as fillers is at about 10%. Among the five stable plastics, fillers are largely used in polyvinyl chloride (PVC) and polypropylene (PP). For instance, the content of filler could reach more than 50% that of the total resins of rigid PVC plastics used to manufacture plastic-steel door and windows, pipes, tiles, etc.

Today, synthetic polymeric materials have shown some properties quite similar to those of steel and iron, wood and cement. During 1980s, the world market for plastic

increased by 62%, while the market for steel and iron decreased by 21%. In 1996, the world capacity of synthetic resins reached 157 million metric tons (MMT) with the productive output of 129 MMT. In developing countries, the demand for synthetic materials grows even more rapidly. PVC is the oldest thermoplastic with wide areas of application and low cost. Currently PVC has become the second largest commodity plastic after polyethylene. The world production in 1997 was estimated to be around 23 million tones. Globally, PVC has 20% of plastic market share and is the second largest in terms of variety.

The PVC plastic was first commercially produced in Europe in the 1930s and in the past 60 years it has undergone continuous development and improvement. Before PVC can be made into products, it has to be combined with a range of special additives. The essential additives for all PVC materials are heat stabilisers and lubricants. In the case of flexible PVC, plasticisers are also incorporated. Other additives which may be used include fillers, processing aids, impact modifiers and pigments. Once the additives have been selected, they are mixed with the polymer (PVC) in a process called compounding. The resultant blend is then fed into the processing equipment which include extrusion, injection moulding, blow moulding, spreading and coating.

Along with the development of chemical construction materials, rigid-PVC has found more uses, for example in making door, windows, draining pipes etc. The chemistry of PVC has been understood since the end of the last century. It is the world's most researched plastic and polymer.

Contrary to soft-plastics, mineral fillers to be used in rigid-plastics have to be compounded with synthetic resins, in order to improve the mechanical strength and to reduce cost. Many minerals have been used as fillers but calcium carbonate has the largest market share. However, because of improper and poor compatibility between synthetic polymers and mineral fillers, they are hard to process and the resultant plastics give bad performance.

The fillers are commonly used are calcium carbonate and talc. Coupling agents, surfactants and polymers are often used to chemically treat the surface of fillers to improve the compatibility between resins and inorganic fillers, and then the processing and mechanical properties of the material. In PVC/CaCO₃ system, titanates are the most often used surface modifiers.

To improve the compatibility, a coupling agent is usually introduced to reduce the surface energy of mineral fillers, thus leading to a better molecular dispersion in the resins. The first silicon coupling agent, RSiX₃, was commercialized by Union Carbide (USA) in 1940s, whereas Cavedon Chemicals (USA) have developed the organic titanates and zircoaluminates separately.

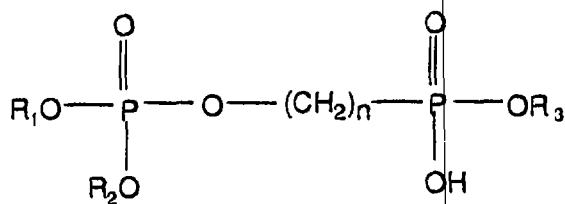
However, when organic titanates are used as coupling agent, some problems remained. For example, many titanates are oily material with high viscosity therefore it is difficult to cover the surface of fillers homogeneously during the mixing stage. Furthermore titanates will decompose if water is present in the fillers. Besides, the cost of titanates is still very high.

Another way of surface modification is to use surfactant. Because of its amphoteric character, hydrophilic group may adsorb a surfactant on the surface of fillers with its hydrophobic chain pointing outside. Some oleochemical based surfactants such as fatty acid and fatty ammonium salts have been used as modifier but usually they can not provide the performance as well as the present coupling agent can. Probably, these oleochemicals with mono-functional group can not be adsorbed on the surface of the fillers effectively.

SUMMARY OF THE INVENTION

Accordingly, there is provided a process to synthesise multi-functional groups oleochemicals, the process consists the steps of a) reacting a phosphoryl halide with a diol at a temperature selected from 10 °C to room temperature, under vacuum selected from 10 mmHg to 760 mmHg, to form an intermediate, b) reacting the intermediate with a fatty alcohol of a desired chain length at a temperature selected from 30 to 70 °C, under vacuum selected from 10 mmHg to 760 mmHg, and c) reacting the resultant mixture of (b) with an alcohol in a presence of a suitable catalyst with 0.5 to 2 %w at a temperature selected from 50 to 90°C, under vacuum selected from 10 mmHg to 760 mmHg.

Further, there is provided alkyl diisopropyl diphosphates (ADDP) which is an ester which contain a hydroxyl group and alkoxy groups of different number of carbons, ranges from C1 to C24, branched or straight chain, having a general structure



wherein n is 2,4,6....., R₁, R₂ and R₃ are alkyl groups.

Also provided is a process of formulating a polymer using oleochemicals, the oleochemicals are produced by the following steps of reacting a phosphoryl halide with a diol at a temperature selected from 10 °C to room temperature, under vacuum selected

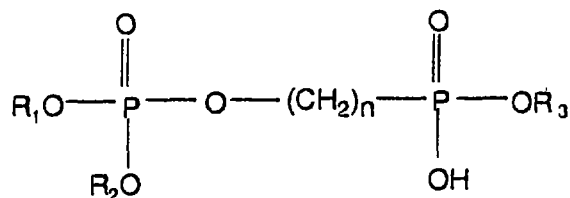
from 10 mmHg to 760 mmHg to form an intermediate, reacting the intermediate with a fatty alcohol of a desired chain length at a temperature selected from 30 to 70 °C, under vacuum selected from 10 mmHg to 760 mmHg; reacting the resultant mixture of (b) with an alcohol in a presence of a suitable catalyst with 0.5 to 2 %w at a temperature selected from 50 to 90 °C, under vacuum selected from 10 mmHg to 760 mmHg to form the oleochemicals, stirring a filler such as calcium carbonate (CaCO_3) in a container, placed in an oil-bath and heated to 135 to 150 °C, preferably at 140 °C, mixing and stirring the oleochemicals into the filler from step (d) to form a modified filler, cooling the modified filler obtained from step (e), blending the polymer resin with additives such as dioctyl phthalate, tribasic lead sulphate, dibasic lead phosphate and lead stearate, heating the mixture obtained from step (g) to 80 to 85°C, preferably 80 °C, adding some preferred additives such as stearic acid, calcium stearate and paraffin into the mixture obtained from step (h), heating the mixture obtained from step (h) to 85 to 95°C, preferably 90°C, mixing the modified filler into the mixture obtained from step (j), heating the mixture obtained from step (k) to 100 to 110°C, preferably 105°C, cooling the mixture obtained from step (l), preferably to room temperature, and blending the resultant product from step (m) into suitable machinery to form polymer sheets.

The present invention consists of certain novel features and a combination of parts hereinafter fully described and particularly pointed out in the appended claims, it being understood that various changes in the details may be without departing from the scope of the invention, or sacrificing any of the advantage of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention relates to the synthesis of oleochemicals with multi-functional groups, the oleochemicals and their uses. Hereinafter, this specification will describe the present invention according to the preferred embodiment. However, it is to be understood that limiting the description to the preferred embodiment of the invention is merely to facilitate discussion of the present invention and it is envisioned that those skilled in the art may devise various modifications and equivalents without departing from the scope of the appended claims.

According to the preferred embodiment of the present invention, multi-functional oleochemicals containing phosphate group are synthesised in a three-steps reaction, the general structure of the oleochemicals can be represented by



wherein n is 2,4,6.....

R₁, R₂ and R₃ are alkyl groups

In the first step, phosphoryl chloride (POCl₃) is cautiously reacted with 1,6-hexylene glycol at low temperature, preferably at about 15°C. The hydrogen chloride (HCl) gas

evolved is trapped and bubbled into sodium hydroxide (NaOH) solution. The pH of the solution is monitored and after it remained unchanged, the reaction can be considered to be complete.

In the second step, fatty alcohol of a desired chain length is then added to the resultant mixture and the reaction temperature is slowly raised to 35 to 40°C. The completion of this step is also monitored in the manner described earlier.

Then isopropyl alcohol is added and the reaction mixture allowed to react further at 60 to 80°C. The progress of the third step is also indicated by the pH of the NaOH solution. All steps involve the release of HCl throughout the reaction.

The reaction involving POCl_3 has to be carried out at a low temperature otherwise its reaction with 1,6-hexylene glycol would be too vigorous. It is also observed that excess amount of POCl_3 will give product of slightly dark colour.

Since this invention involves a multi-step process, analysis of yield of products is found to be slightly complex. The determination of yield is estimated through the released HCl gas, which is bubbled (absorbed) into NaOH, where the acidic solution is back-titrated with a known concentration of NaOH solution. However it is worthy to note that sometimes it is quite difficult to monitor the HCl gas released during the reaction, which can affect the calculation of yield.

In this invention, three types of fatty alcohols derived from palm oil are used in the synthesis: C14, C16, C18 fatty alcohols. It has to be envisaged that any type of vegetable oils can be used as the source of fatty alcohols. The oleochemicals obtained from these alcohols differ slightly, where C14 alcohol gives a viscous liquid, C16 alcohol gives a solid to semi-solid and C18 gives a solid product (paste form).

The reactions can be carried under vacuum selected from 10 mmHg to 760 mmHg (1 atm), but at 1atm, the reaction period has to be prolonged. Several reaction parameters are studied involving temperature, duration of reaction, effects of mole ratio of reactants and effects of catalysts.

Effect of Temperature

In step 1, the reaction between POCl_3 and 1,6-hexylene glycol is an exothermic reaction, that a lower reaction temperature is favourable. The range of temperature can be from 10 °C to room temperature, preferably from 10 to 20 °C. The second step is also found to be vigorous and 30 to 70°C is found to be the suitable temperature range, preferably from 35 to 50 °C. For step 3, the influence of temperature on yield is investigated under the following reaction condition: POCl_3 : 1,6-hexylene glycol : cetyl alcohol : isopropyl alcohol = 2 : 1 : 1:2 (mole ratio). The reaction time is 3 hours, in the presence of 1.0% catalyst (wt). The recommended reaction temperature is between 50 to 90°C, preferably from 60 to 80 °C.

Table 1: The effect of temperature on the yield

Reaction temperature, °C	50	60	70	80	90
Yield(%)	86.50	90.73	92.74	91.30	88.36
Colour	White	White	White	White	yellowish

Effect of Reaction Time

For steps 1 and 2, the periods of reaction are fixed at 40 and 60 minutes, respectively. For step 3, influence of reaction time is investigated under similar reaction conditions as above and temperature at 60°C. Based on the study, 2.5 to 3.5 hours of reaction time are recommended. The reaction time can vary depending on the vacuum applied. In step 1, the time can vary from about 40 minutes to about 3 hours. In step 2, from about 1 hour to 4 hours, whilst in step 3, from about 2 hours to 5 hours.

Table 2: The effect of reaction time on the yield

Reaction time hrs	2.0	2.5	3.0	3.5	4.0
Yield, %	85.17	88.29	90.73	91.03	90.58
Colour	White	White	White	Yellowish	Yellowish

Effect of Mole Ratio of Starting Materials

For fast reactions, such as in steps 1 and 2, theoretical mole ratio of the starting materials or reagent is best to be followed, as excess will cause problem of separation.

For step 3, influence of mole ratio of POCl_3 to isopropyl alcohol is investigated at reaction conditions: $T = 60^\circ\text{C}$, time 3 hours and catalyst 1.0wt%.

Table 3: Effect of mole ratio of starting materials on the yield

POCl_3 : isopropyl alcohol (mol:mol)	1 : 1	1 : 1.2	1 : 1.4	1 : 1.6	1 : 1.8
Yield %	85.79	88.13	91.09	91.58	91.49

When more isopropyl alcohol is used, an increase in percent yield is observed. However, tri-isopropyl diphosphate, a by-product of the reaction is also expected to be formed. Therefore, mole ratio of 1:1.6 is recommended.

Effect of Catalyst

For step 3, three catalysts are compared under the following reaction conditions: POCl_3 : 1,6-hexylene glycol : cetyl alcohol : isopropyl alcohol = 2 : 1 : 1 : 3, $T = 60^\circ\text{C}$, time is 3 hours and catalyst 1.0 wt%.

Table 4: Effect of catalyst on the yield

Catalyst	None	MgCl_2	AlCl_3	$\text{Ti}(\text{OC}_2\text{H}_5)_4$
Yield %	83.29	85.40	91.23	90.73

Table 5: Effect of catalyst on the yield

Catalyst, %(wt)	0.5	0.7	0.9	1.1	1.3
Yield %	85.01	88.30	90.19	91.58	91.79

As seen from the results in Table 4, both AlCl_3 and $\text{Ti}(\text{OC}_2\text{H}_5)_4$ give high and comparable yield. The influence of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ in the reaction is further investigated. The appropriate amount of catalyst is found to be from about 0.5 to 2% (based on the weight of POCl_3), preferably about 0.9 to 1.3%, (based on the weight of POCl_3). As shown in Table 5, the percentage by weight of the catalyst also enhances the percentage of yield obtained.

Effect of Vacuum

From steps 1 to 3, the reaction temperature is increased gradually, as well as the released of HCl . The vacuum of the reaction system should be increased gradually as the released HCl can absorb some amount of POCl_3 , which will result in low yield (conversion). The processes can be carried out under vacuum selected from 10 mmHg to 760 mmHg.

Effect of Rate of Agitation

The rate of agitation should be at a minimum, otherwise a lot of foam will form and some of the POCl_3 will be lost.

EXAMPLES

Example 1

A four-neck round bottom flask is used as a reactor equipped with additional funnel, thermometer, condenser and stirrer. About 11.8g, 0.1 mol of 1,6-hexylene glycol is placed and the reactor is immersed in a water bath and the temperature maintained below 15°C. The vacuum of reactor is controlled to be at 10 to 15 mmHg. 18.5ml, 0.2mol of POCl_3 is added dropwise and reaction temperature allowed and maintained at 15°C. The released HCl is absorbed by NaOH solution. When the pH value of NaOH solution remained constant, the first step is considered to be complete. Then 24.3g of C_{16} -alcohol are added slowly and reaction temperature is raised to 35 to 40°C to proceed to step 2. When the pH value of NaOH solution became constant, step 2 is considered to be complete. Then, 15.2 ml, 0.2mol of isopropyl alcohol and a small amount of catalyst are added, while the temperature of the water bath is raised to 60 to 80°C. When the pH value of NaOH remained constant again, step 3 is considered to be complete. The obtained product is transferred and distilled under 5mmHg vacuum. The distillate is washed 2 to 3 times with warm dilute sulfuric acid and then 3 to 4 times with hot water. The product is then cooled and dried under vacuum.

Example 2

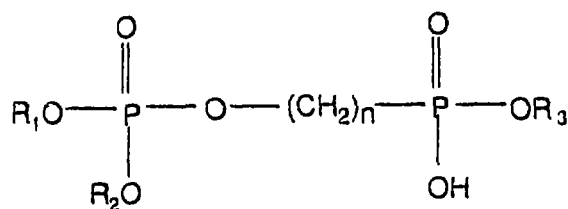
In a similar set-up, 11.8g, 0.1mol of 1,6-hexylene glycol is placed in the reaction vessel and cooled to temperature at 15°C. In an attached additional funnel, 18.5ml, 0.2mol of POCl_3 is added in portions to the alcohol, and allowed to react and the temperature maintained at 15°C. After the addition process is complete, the mixture is allowed to

react at that temperature for another 15 minutes followed by at least another 150 minutes at room temperature. The released HCl gas is bubbled into NaOH solution and the pH checked until remained unchanged. Then 24.3g of C₁₆-alcohol is added slowly and reaction temperature is raised to 35 to 40°C to proceed to step 2. When the pH remained constant, then, 15.2 ml, 0.2mol of isopropyl alcohol and a small amount of catalyst are added and the temperature raised to 60 to 80°C. The completeness of the reaction is also monitored through the pH readings.

Example 3

The product obtained from the reaction is purified by column chromatography using a stationary phase Kieselgel 60 (70 to 230 mesh ASTM) and a mobile phase hexane:ether (80:20) or by gradient elution.

The multi-functional groups oleochemical obtained from the above-mentioned process is an alkyl diisopropyl diphosphates (ADDP) which is an ester which contain a hydroxyl group and alkoxy groups of different number of carbons. As illustrated above, the general formula can be represented by



wherein n is 2,4,6.....

R₁, R₂ and R₃ are alkyl groups

ADDP, a synthetic product of fatty alcohol and POCl_3 , has one hydrophilic and several hydrophobic groups in its structure. For example, ADDP derived from C16 fatty alcohol is white or pale yellow solid, having a melting point (m.p.) of 60 to 62°C and easily dissolved in water ($\text{pH} < 2.0$). The aqueous solution of ADDP is stable and could be used directly. The hydrophilic group of ADDP allows ADDP to be better absorbed onto the surface of the filler and the hydrophobic chain allows better mixing with the PVC resin. Therefore a homogenous mixture of fillers and PVC resin is obtained. A mono-functional groups oleochemicals such as fatty acid and fatty ammonium salt which have been used as modifier do not give performance as well as ADDP.

Now, the uses of ADDP in the manufacture of polymers, in particular plastic will be described. In the preferred embodiment of the invention, the plastic is PVC.

Prior to the PVC formulation, ADDP is usually premixed with the calcium carbonate. In the laboratory, a certain amount of CaCO_3 is stirred in an appropriate container or flask and placed in an oil-bath and heated to 140°C. After 10 minutes, the required amount of ADDP added and stirred at the above temperature for another 10 minutes. The sample is then taken out, cooled and kept in a dessicator. At industrial scale, a high speed mixer is used to carry the filler, where the mixer is heated to 140°C and a certain amount of the modifier is added.

The type of PVC obtained will depend on the formulation chosen. For example, rigid PVC can be obtained blending a certain amount of PVC resin with dioctyl phthalate, which are fed into a high speed mixer and allowed to mix well for 5 minutes. Other

additives such as tribasic lead sulphate, dibasic lead phosphite and, lead stearate are added and the mixture heated to 80°C with agitation. Some other additives such as stearic acid, calcium stearate and paraffin are later added and the agitation continued until the temperature reaches about 90°C. The modified CaCO_3 is then poured in and the temperature of the mixer is raised to 105°C. The total mixing period is about 25 minutes. The resultant mixture is then cooled at room temperature. It is then ready to be made into PVC sheets where it will be blended in a rolling mill. The gap between the rollers will determine the thickness of the sheet. Then it is process further before some physical testing measurements such as tensile strength, impact strength and elongation at break are carried out.

PVC, calcium carbonate and organic titanate are industrial products. Other materials such as C_{16} alcohol, P_2O_5 , POCl_3 , glycols are chemical reagents. Deionised water is used.

Dry method is applied in modification of CaCO_3 . The filler is put into 250 ml round flask, heated to 130°C under stirring and kept warming for 10 minutes. After certain amount of ADDP (or other modifiers) is added, kept stirring for another 10 minutes. The ADDP is then cooled to room temperature and put into desiccator.

Powder CaCO_3 is kept under 20MPa pressure for 5 minutes to form a pellet. Erma G-1 Contact Angle Instrument is applied to detect the contact angle against water or liquid paraffin. The apparent viscosity can be detected by homogeneously mixing of CaCO_3 and liquid paraffin at a ratio of 1:2 (w/w) before introduced into a rotating viscometer at

room temperature. Oil absorptivity is evaluated according to Chinese Standard GB1717-79 whilst the whiteness is evaluated according to Chinese Standard GB4794-84, by 2BD whiteness meter.

To evaluate mechanical properties of PVC plastics, sample preparation and detection are using the methods as followed, tensile strength is evaluated according to Chinese Standard GB1040-92, extension at break is evaluated according to Chinese Standard GB1040-92 and impact strength is evaluated according to Chinese Standard GB1043-93.

The rheological properties of PVC samples are detected by RC-90 Torque Rheometer under following conditions, temperature of 175°C, load of 5kg, rotating speed of 30rpm and sample weight of 65g.

Surface modification of CaCO₃

Contact angle.

Contact angle is one of the mostly used parameters to reflect the wetting property of solid/liquid interface. The values for pure and modified CaCO₃ with kinds of modifiers are listed in Table 6.

Table 6: Contact angle of CaCO_3 , amount of modifiers: 0.7% w

Modifier	Contact angle ($^\circ$)	
	Against water	Against liquid paraffin
None	15	20
ADDP	98	10
C_{16} -alkyl phosphate ester	83	18
Mono C_{16} -alkyl glycerophosphate	85	12
Titanate (NDZ-201)*	75	11

*As reference

From Table 6, it could be seen that all modifiers could increase the contact angle of CaCO_3 against water and decrease that against liquid paraffin. Among all, ADDP had the most obvious effect.

Oil absorbility.

Oil absorbility demonstrates the amount of plasticiser that can permeate into the space among CaCO_3 particles. This part of plasticiser could not function as plasticisation, thus it should be cut as possible. From Table 7, the oil absorbility of all modified CaCO_3 decreased and ADDP behaved the best.

Table 7: Oil absorbility of modified CaCO_3 , amount of modifiers: 0.7% w

Modifier	oil absorbility, ml/g CaCO_3				%
	1	2	3	average	
None	0.82	0.80	0.81	0.81	100
ADDP	0.32	0.33	0.32	0.32	39.5
C_{16} -alkyl phosphate	0.47	0.45	0.47	0.47	58.0
ester					
Mono C_{16} -alkyl	0.56	0.58	0.55	0.57	70.3
glycerophosphates					
Titanate (NDZ-201)	0.45	0.45	0.46	0.45	55.6

Viscosity.

Viscosity of a paste of filler/liquid paraffin is used to evaluate the mobility and dispersing property of fillers in resins. Some data in Table 8 showed that modifiers could significantly drop the viscosity of system, also ADDP is the best.

Table 8: Viscosity of modified CaCO₃, amount of modifiers: 0.7% w, T = 25°C

Modifiers	Viscosity, mPaS					%
	1	2	3	4	Average	
None	2100	2400	2400	2600	2300	100
ADDP	82	85	80	85	85	4.13
C ₁₆ -alkyl phosphate ester	118	120	105	120	116	5.04
Titanate (NDZ-201)	110	110	110	110	110	4.78

Whiteness.

Whiteness of samples is shown in Table 9, where pure CaCO₃ had the highest value. When covered with modifiers, whiteness decreased. Titanate itself had deeper colour, thus made whiteness dropped by 7.4%, while ADDP only 0.4%.

Table 9: Whiteness of modified CaCO₃, amount of modifiers: 0.7% w

Samples	pure CaCO ₃	ADDP	C ₁₆ -alkyl phosphate ester	Titanate (NDZ-201)
Whiteness	91.2	90.8	87.8	84.5
%	100	99.6	96.3	92.6

Through the above tests, it could be seen that to CaCO₃, ADDP, is a kind of modifier with good properties. Differential Scanning Calorimeter (DSC) test showed that ADDP

modified CaCO_3 had good heat resistance, with peak of heat absorption appeared at above 300°C , while these modified with titanate appeared earlier at 260°C .

Mechanical property of PVC/ CaCO_3

Tensile strength.

Three different amount of CaCO_3 are added in PVC plastics with the same formulation. Data of tensile strength are shown in Table 10. PVC plastics without CaCO_3 had tensile strength of 50.1Mpa. The value dropped along with the increment of amount of CaCO_3 . For example, when CaCO_3 is 50%, tensile strength is 33.1Mpa, decreased by 33.9%. On the other hand, those containing various modifiers had increased tensile strength to some extent. This improvement is obvious especially for samples with lower content of CaCO_3 . For instance, when content of CaCO_3 is 30%, tensile strength of sample modified by ADDP is 42.4Mpa, increased by 9.6% of the one without modifier (38.7 Mpa), while that containing titanate only increased by 3.9%.

Table 10: Tensile strength of rigid PVC, amount of modifiers: 0.4% w. Unit: Mpa

Content of CaCO_3 , %*	Modifier				
	-	ADDP	C_{16} -alkyl phosphate ester	Mono C_{16} -alkyl glycerophosphate	Titanate
0	50.1				
30	38.7	42.4	39.6	39.5	40.2
50	33.1	36.7	36.0	35.6	35.2
67	30.9	30.9	31.4	30.7	30.5

*PVC resin amount is considered as 100%.

Extension at break.

From Table 11, it could be seen that when CaCO_3 content increased, the plasticity of samples dropped and brittleness increased, resulting in lowering of extension at break. On the other hand, extensions at break are all increased with modified fillers. Same as tensile strength, modification effect is more obvious with lower CaCO_3 content.

Table 11: Extension at break of rigid PVC amount of modifiers: 0.4% w

Content of CaCO_3 , %*	Modifier				
	-	ADDP	C_{16} -alkyl phosphate ester	Mono C_{16} -alkyl glycerophosphate	Titanate
30	54	96	102	76	76
50	46	58	58	46	50
67	22	21	20	20	22

* Extension at break of PVC before being extended is considered as 0 %.

Impact strength.

From the view of practical application, impact strength is one of important parameters of mechanical property of plastics.

Table 12: Impact strength of rigid PVC amount of modifiers: 0.4% w

Unit: KJ/m^2

Content of		Modifier			
CaCO_3 , %*	-	ADDP	C_{16} -alkyl	Mono C_{16} -alkyl	Titanate
			phosphate ester	glycerophosphate	
0	8.7				
30	8.9	10.6	10.9	9.6	10.9
50	10.1	12.3	11.8	10.9	12.1
67	8.12	8.36	8.42	8.39	8.37

From Table 12, the impact strength of PVC plastics without CaCO_3 is 8.7 KJ/m^2 . When filled with CaCO_3 , plasticity of PVC dropped but hardness increased, thus impact strength increased as well. When CaCO_3 content is 50%, impact strength reached the optimum value (10.1 KJ/m^2). But if CaCO_3 content continued to grow, increment of brittleness would lead to drastic dropping of impact strength. On the other hand, at each level of CaCO_3 content, all modifiers could improve impact strength of samples. As when CaCO_3 content is 50%, impact strength of system with ADDP increased by 22%, compared to those without modifiers, while titanate increased by 20%.

The above experiments demonstrated that CaCO_3 modified by ADDP had excellent compatibility with PVC resins and other formulated components. The mechanical strength of materials could be improved evidently.

Processing properties of PVC/ CaCO₃

The rheological performances of samples are tested. Results are shown in Table 13.

Table 13: Rheological property of rigid PVC/CaCO₃ plastics amount of modifiers:

0.4% w, CaCO₃:PVC = 50:100 (w/w)

PVC samples	Plasticising time, S	Balanced torque, Nm	Maximum torque, Nm
No modifier	96	11	15.1
ADDP	78	8.71	13.2

When CaCO₃ is modified by ADDP, plasticising time, balanced torque and maximum torque dropped by 18.8%, 20.1% and 12.6% respectively. Dropping of plasticising time means that the shortening of processing time of PVC plastics. This is beneficial to heat stability of PVC plastics and the production efficiency can be increased. Decrement of balanced torque and maximum torque could be attributed to surfactants, which improved the compatibility between PVC resins and fillers, reduced the cohesive energy, resulting in better processing property.

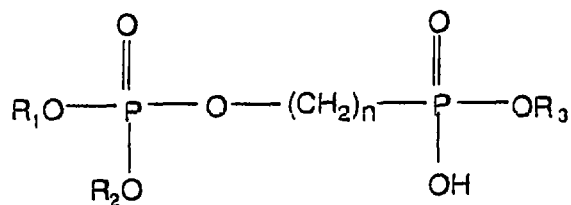
While in the foregoing specification this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.

CLAIMS

1. A process to synthesise multi-functional groups oleochemicals, the process consists the steps of:
 - a) reacting a phosphoryl halide with a diol at a temperature selected from 10 °C to room temperature, under vacuum selected from 10 mmHg to 760 mmHg, to form an intermediate;
 - b) reacting the intermediate with a fatty alcohol of a desired chain length at a temperature selected from 30 to 70 °C, under vacuum selected from 10 mmHg to 760 mmHg; and
 - c) reacting the resultant mixture of (b) with an alcohol in a presence of a suitable catalyst with 0.5 to 2 %w at a temperature selected from 50 to 90 °C, under vacuum selected from 10 mmHg to 760 mmHg.
2. The process of claim 1, wherein the phosphoryl halide is phosphoryl chloride (POCl_3).
3. The process of claim 1, wherein the diol is 1,6-hexylene glycol.
4. The process of claim 1, wherein the hydrogen chloride (HCl) gas evolved in step (a) is trapped and bubbled into sodium hydroxide (NaOH) solution.
5. The process of claim 1, wherein the reaction temperature in step (a) is selected from 10 to 20 °C.

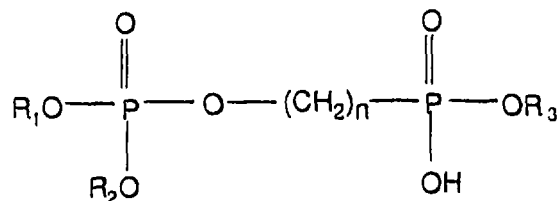
6. The process of claim 1, wherein the pH of the solution of step (a) is monitored and after it remained unchanged, the reaction can be considered to be complete.
7. The process of claim 1, wherein the desired chain length of the fatty alcohol is C14, C16 and C18, preferably C16 and C18.
8. The process of claim 1, wherein the reaction temperature in step (b) is selected from 35 to 50 °C.
9. The process of claim 1, wherein the pH of the solution of step (b) is monitored and after it remained unchanged, the reaction can be considered to be complete.
10. The process of claim 1, wherein the reaction temperature in step (c) is selected from 60 to 80 °C.
11. The process of claim 1, wherein the catalyst in step (c) is selected from MgCl_2 , AlCl_3 , $\text{Ti}(\text{OC}_2\text{H}_5)_4$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$.
12. The process of claim 1, wherein the catalyst having 0.9 to 1.3%w.
13. The process of claim 1, wherein the pH of the solution of step (c) is monitored and after it remained unchanged, the reaction can be considered to be complete.

14. The process according to any one of the preceding claims, wherein hydrogen chloride (HCl) gas is released throughout steps (a), (b) and (c).
15. The process according to any one of the preceding claims, wherein the mole ratios of starting materials should be in the range between 1 to 3 with respect to number of mole of POCl_3 , preferably between 1 to 2.
16. The process according to any one of the preceding claims, wherein the source of fatty alcohols is from any vegetable oils, preferably palm oil.
17. The process according to any one of the preceding claims, wherein the multi-functional groups are phosphate, hydroxyl and several alkoxy groups.
18. The process according to any one of the preceding claims, wherein the oleochemicals such as alkyl diisopropyl diphosphates (ADDP) which is an ester which contain phosphates, a hydroxyl group and alkoxy groups of different number of carbons, ranges from C1 to C24, either branched or straight chained having a general structure



wherein n is 2,4,6....., R_1 , R_2 and R_3 are alkyl groups are obtained.

19. Alkyl diisopropyl diphosphates (ADDP) which is an ester which contain phosphates, a hydroxyl group and alkoxy groups of different number of carbons, ranges from C1 to C24, either branched or straight chained having a general structure



wherein n is 2,4,6,....., R₁, R₂ and R₃ are alkyl groups.

20. The ADDP as claimed in claimed 19, wherein the ADDP derived from C16 fatty alcohol is a white or pale yellow solid.
21. The ADDP as claimed in claimed 20, wherein the ADDP having the melting point (m.p.) of 60 to 62°C.
22. The ADDP as claimed in claimed 20, wherein the ADDP dissolves in water (pH<2.0).
23. The ADDP as claimed in claimed 20, wherein the aqueous solution of ADDP is stable and could be used directly.

24. A process of formulating a polymer using oleochemicals, the oleochemicals are produced by the following steps:

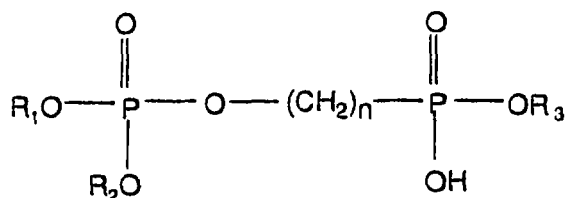
- a) reacting a phosphoryl halide with a diol at a temperature selected from 10 °C to room temperature, under vacuum selected from 10 mmHg to 760 mmHg to form an intermediate;
- b) reacting the intermediate with a fatty alcohol of a desired chain length at a temperature selected from 30 to 70 °C, under vacuum selected from 10 mmHg to 760 mmHg;
- c) reacting the resultant mixture of (b) with an alcohol in a presence of a suitable catalyst with 0.5 to 2 %w at a temperature selected from 50 to 90 °C, under vacuum selected from 10 mmHg to 760 mmHg to form the oleochemicals;
- d) stirring a filler such as calcium carbonate (CaCO_3) in a container, placed in an oil-bath and heated to 135 to 150 °C, preferably at 140 °C;
- e) mixing and stirring the oleochemicals into the filler from step (d) to form a modified filler;
- f) cooling the modified filler obtained from step (e);
- g) blending the polymer resin with additives such as dioctyl phthalate, tribasic lead sulphate, dibasic lead phosphate and lead stearate;
- h) heating the mixture obtained from step (g) to 80 to 85 °C, preferably 80 °C;
- i) adding some preferred additives such as stearic acid, calcium stearate and paraffin into the mixture obtained from step (h);
- j) heating the mixture obtained from step (h) to 85 to 95 °C, preferably 90 °C;
- k) mixing the modified filler into the mixture obtained from step (j);
- l) heating the mixture obtained from step (k) to 100 to 110 °C, preferably 105 °C;

- m) cooling the mixture obtained from step (l), preferably to room temperature; and
- n) blending the resultant product from step (m) into suitable machinery to form polymer sheets.

25. The process as claimed in claim 24, wherein the filler is calcium carbonate (CaCO_3).

26. The process as claimed in claim 24, wherein the polymer is plastic, preferably polyvinyl chloride (PVC).

27. The process as claimed in claim 24, wherein the oleochemicals is alkyl diisopropyl diphosphates (ADDP) which is an ester which contain phosphates, a hydroxyl group and alkoxy groups of different number of carbons, ranges from C1 to C24, either branched or straight chained having a general structure



wherein n is 2,4,6....., R_1 , R_2 and R_3 are alkyl groups are obtained.

28. The process of claim 24, wherein the phosphoryl halide is phosphoryl chloride (POCl_3).

29. The process of claim 24, wherein the diol is 1,6-hexylene glycol.

30. The process of claim 24, wherein the hydrogen chloride (HCl) gas evolved in step (a) is trapped and bubbled into sodium hydroxide (NaOH) solution.
31. The process of claim 24, wherein the reaction temperature in step (a) is selected from 10 to 20 °C.
32. The process of claim 24, wherein the pH of the solution of step (a) is monitored and after it remained unchanged, the reaction can be considered to be complete.
33. The process of claim 24, wherein the desired chain length of the fatty alcohol is C14, C16 and C18, preferably C16 and C18.
34. The process of claim 24, wherein the reaction temperature in step (b) is selected from 35 to 50 °C.
35. The process of claim 24, wherein the pH of the solution of step (b) is monitored and after it remained unchanged, the reaction can be considered to be complete.
36. The process of claim 24, wherein the reaction temperature in step (c) is selected from 60 to 80 °C.
37. The process of claim 24, wherein the catalyst in step (c) is selected from MgCl_2 , AlCl_3 , $\text{Ti}(\text{OC}_2\text{H}_5)_4$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$.

38. The process of claim 24, wherein the catalyst having 0.9 to 1.3%w.
39. The process of claim 24, wherein the pH of the solution of step (c) is monitored and after it remained unchanged, the reaction can be considered to be complete.
40. The process according to any one of claims 24 to 39, wherein hydrogen chloride (HCl) gas is released throughout steps (a), (b) and (c).
41. The process according to any one of claims 24 to 40, wherein the mole ratios of starting materials should be in the range between 1 to 3 with respect to number of mole of POCl_3 , preferably between 1 to 2.
42. The process according to any one of claims 24 to 41, wherein the source of fatty alcohols is from any vegetable oils, preferably palm oil.
43. The process according to any one of claims 24 to 42, wherein the multi-functional groups are phosphates, hydroxyl, and alkoxy groups of different number of carbons, ranges from C1 to C24, either branched or straight chained.